DFT Studies of the Organocatalytic Aldol Reaction and a Frustrated Lewis Pair

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Abstract

The computational study, and in particular the density functional theory (DFT) study of the organocatalytic α-chlorination-aldol reaction and the chiral backbone Frustrated Lewis Pair (FLP) system served as a valuable tool for experimental purposes.

This thesis describes methods to consider different transition states of the proline-catalyzed α-chlorination aldol reaction to determine the reasonable transition state in the reaction between the enamine and α-chloro aldehydes. Moreover, the novel intramolecular Frustrated Lewis pair based on a chiral backbone for the asymmetric hydrogenation of imines and enamines was designed and the ability of hydrogen splitting by this new FLP system was examined by computational modeling and calculating the hydrogen activation energy barrier.

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Abbreviations and symbols

Ac	Acetyl
Ar	Aryl
AIM	Atoms-in-molecules
atm	atmosphere
BCP	Bond critical point
d	Days
DCE	1,2-dichloroethane
DFT	Density functional theory
DMF	*N*,*N*-dimethylformamide
DMSO	Dimethyl sulfoxide
DKR	Dynamic Kinetic Resolution
ee	Enantiomeric excess
FLPs	Frustrated Lewis Pairs
G_b	Kinetic energy density
h	Hour
H_b	Total electron energy density
IEFPCM model	Integral equation formalism variant of the polarizable continuum
LUMO	Lowest unoccupied molecule orbital
HOMO	Highest occupied molecule orbital
NBO	Natural bond orbital

NCS	*N*-chlorosuccinimide
NMR	Nuclear magnetic resonance
^{n}Pr	n-Propyl
Nu	Nucleophile
Me	Methyl
OAc	Acetoxy
p-TsOH	Para Toluenesulfonic acid
Ph	Phenyl
Pr	Propyl
rt	Room temperature
TBS	tert-butyldimethylsilyl
TIPS	Triisopropylsilyl
TS	Transition state
ρ (r)	Charge density
$\nabla^2\rho$	Laplacian
V_b	Potential energy density

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1 General Introduction

Organocatalysis has drawn attention of a significant group of synthetic chemists. Using organocatalysists is more beneficial than using transition metal catalysts, because of their lack of sensitivity to moisture and oxygen as well as their low cost and low toxicity.

According to the Houck definition, organocatalysis is the catalysis of a reaction by a small organic molecule. By accepted convention, small organic molecule means a molecule without a metal, and not a macromolecule such as protein, nucleic acid, or polymer[1].

Much of the mechanistic understanding of these reactions has come from both computational and experimental investigations. For organic reactions and especially organocatalysis, the structures and energies of transition states are crucial. The energy difference of related transition states can show chemists which reaction pathway is most likely and could give them information on activation barriers of the reaction. Quantum mechanical calculations, and in particular density functional theory (DFT), can be used to study these properties.

Transition state structures are not directly observable by experiment, but DFT calculations of small to intermediate systems have become very fast and can be carried out within hours or days on standard personal computers. In other words, DFT methods can be used to describe a large number of organocatalytic systems well.

Over the past two decades, DFT has become a substantial method for studying large chemical systems with high accuracy.[2] The dispersion interaction principle from electron correlation through space is described inadequately by conventional DFT methods. However in recent years, DFT methods that explicitly correct for the dispersion interaction or that are implicitly parameterized to describe the dispersion interaction have emerged[3]. Ignoring the dispersion interaction leads to underestimation of interaction energies and overestimation of intermolecular distances. Given this fact, DFT is experiencing continuing developments of new functionals and further improvements.

Breslow and Friesner reported a good predictive quality for the most commonly used DFT functional B3LYP with the 6-31G (d) basis set[4]. They also demonstrated that solvent corrections are able to improve gas phase calculations. Solvent corrections can improve the quality of gas-phase data, if the gas-phase results are already accurate enough. Recent studies have shown that the B3LYP functional is not reliable enough for predicting the reaction energies of certain reactions like homolytic bond breaking reactions or reactions involving transformation between σ and π bonds.[5] There are errors introduced into the B3LYP calculations for very bulky systems due to dispersion energy issues. However, there are some new functionals that take account of dispersion energy in a better way such as B3LYP-D (Grimme) or wB97XD (Head-Gordon).[6]

The wB97XD functional includes empirical dispersion and can better treat hydrogen bonding and van der Waals interactions than conventional DFT.[6]

In order to interpret chemical bonds and their strength in terms of electron density in

different organocatalytic syntheses or analysing and calculating the distribution of electron density in atoms and in bonds between atoms, different computational methods have been used. The possibility of a stereo electronic effect was investigated by using atoms-in-molecules (AIM) theory.[7] In AIM theory, the interaction between two atoms is revealed by the presence of a charge density in the interconnecting space and this charge density is related to a bond critical point (BCP). According to AIM theory, each nucleus in a molecule is surrounded by a region called an atomic basin, which is bounded by a zero-flux surface in the gradient vector field of the charge density $\nabla\rho$ that defines an atomic boundary.[8]

When two atoms share some portion of their surfaces, maximum electronic charge density can be formed between the nuclei, and at the point where the shared surface divides this atomic interaction line there is a saddle point in charge density ρ (r) called a bond critical point (BCP). Therefore, AIM can be used to indicate the existence, or otherwise, of a molecular interaction by identifying a unique line of communication between two chemically interacting nuclei.[9] In AIM theory, the nature of a bonding interaction can be determined through an analysis of the properties of charge density ρ and its Laplacian$\nabla^2\rho$ at the bond critical point (BCP). While the ρ (charge density) value is small, the positive value of $\nabla^2\rho$ (Laplacian) indicates the typical closed-shell kind of interaction and mostly electrostatic interaction. In other words, negative Laplacian at the bond critical point (BCP) stands for all shared-electron (covalent) interactions, while in all closed-shell (electrostatic) interactions cases, there is a positive Laplacian at the bond critical point.[10]

Natural bond orbital (NBO) is the other computational method for analyzing a

many-electron molecular wavefunction in terms of localized electron-pair bonding units. NBO analysis is based on a method for optimally transforming a given wavefunction into localized form, corresponding to the one-center ("lone pair") and two-center ("bond") elements of the chemist's Lewis structure picture.[11] In other words, natural bond orbital (NBO) is used in computational chemistry to calculate the distribution of electron density in atoms and in bonds between atoms.

Having considered the NBO definition, this computational tool has become a powerful and popular method for studying bonding concepts.

As the experimental study of organocatalysis has accelerated significantly, the computational investigations of these reactions have increased in number and function as well. B3LYP with modest basis sets continues to be used routinely for the study of organocatalysis, but deficiencies in this functional have been discovered. This is especially true for reaction thermochemistries and in cases where dispersion effects influence weak interactions between groups. Given this fact, newer and more constructive functionals such as wB97XD are being used routinely. The role of dispersion is likely to be important in controlling stereoselectivities of many reactions, and the addition of dispersion corrections to density functionals is now highly recommended.[12]Computational modeling will continue to complement experimental investigations to provide understanding of organocatalytic reactions.

This thesis is divided into two different parts; A DFT study of the organacatalytic aldol reaction was studied in part one and a DFT study calculating the energy barrier for the chiral Frustrated Lewis pairs system (FLP's) was considered in part two.

2 Part one:

A DFT study of the organacatalytic aldol reaction

Abstract

The asymmetric aldol reaction has been classified as an important subject in organic chemistry. Metal complexes have been shown to catalyze a wide variety of transformations stereoselectively. However, many catalytic metal complexes are highly toxic and expensive and also difficult to remove from products. Hence, as interest in the asymmetric synthesis of chiral molecules is growing, different opportunities for the development of alternative approaches are also being taken into account. Over the last several decades, simple organocatalysts like proline have been shown to be effective in carbon-carbon bond forming reactions.

In this section, the *(S)*-proline catalyzed α-chlorination/aldol reaction, which produces the *syn*-chlorohydrin product in a one-pot one-step procedure, is studied. The observed *syn*-chlorohydrin selectivity is not in accordance with the polar Felkin-Anh model nor the Evans-Cornforth model. Density functional theory calculations revealed that the new Dudding-Britton stereochemical model is able to rationalize the observed *syn*-halohydrin products. Unlike the previous models, the Dudding-Britton model involves avoidance of steric interactions as well as destabilizing electrostatic interactions.

2-1 Introduction

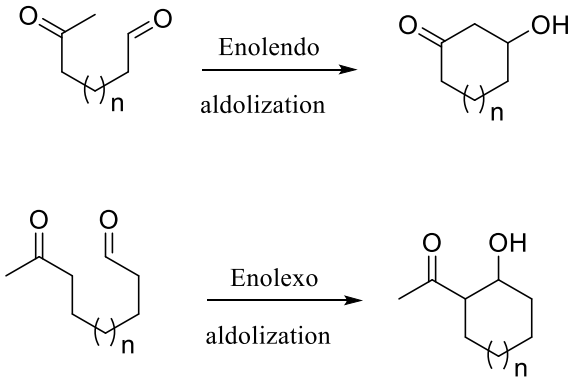
The aldol reaction is one of the most important methods of generating carbon-carbon bonds in organic chemistry[13]. Application of the asymmetric aldol reaction to synthesize chiral building blocks as well as carbohydrates as a class of natural products has been documented.[14,15] In particular, the aldol reactions involving dihydroxy acetone derivatives have great potential to be catalyzed by chiral amines. This fact has been demonstrated by MacMillan, Enders, List and Lerner.[16, 17, 18]

Recently, proline has been found as an efficient catalyst of the direct asymmetric aldol reaction[19]. Proline is capable of transferring chairality as either an iminium electrophile or as an enamine nucleophile[20]. Asymmetric aldol reactions can be divided into intramolecular aldolization and intermolecular aldolization. Quantum mechanical calculations, and in particular density functional theory (DFT), can now be used by experimental chemists to consider real chemical systems. Density functional theory (DFT) has become an efficient method with high precision and accuracy for large chemical systems over the past two decades.[21]

2-2 Enolendo Intramolecular Aldolizations

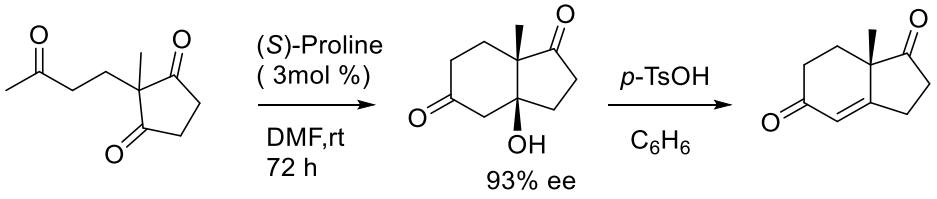
Intermolecular aldolizations are classified into enolendo and enolexo types

(Scheme 1).



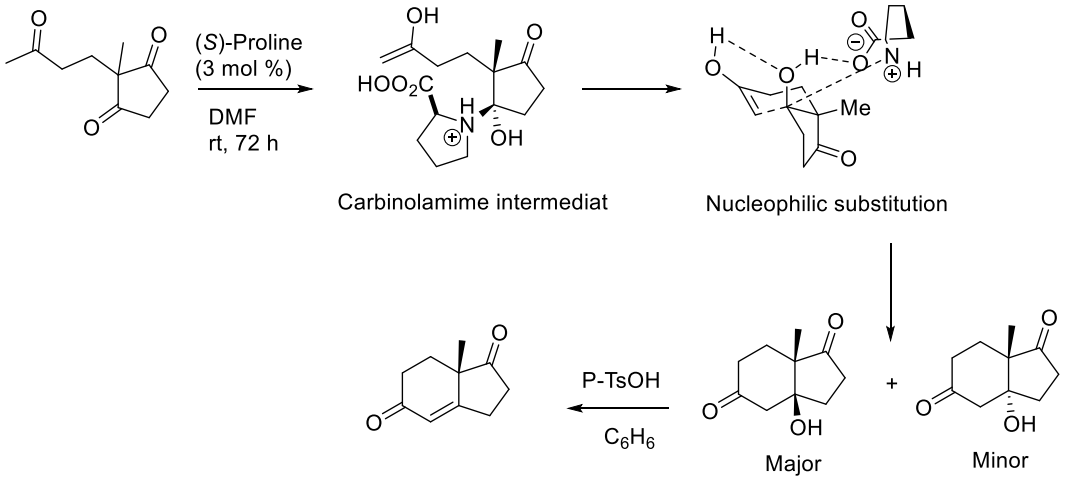
Scheme 1. The two modes of intramolecular aldolization

The Hajos-Parrish-Eder-Sauer-Wiechert reaction reported in 1970[22] is considered as the first enolendo aldolization (Scheme 2).



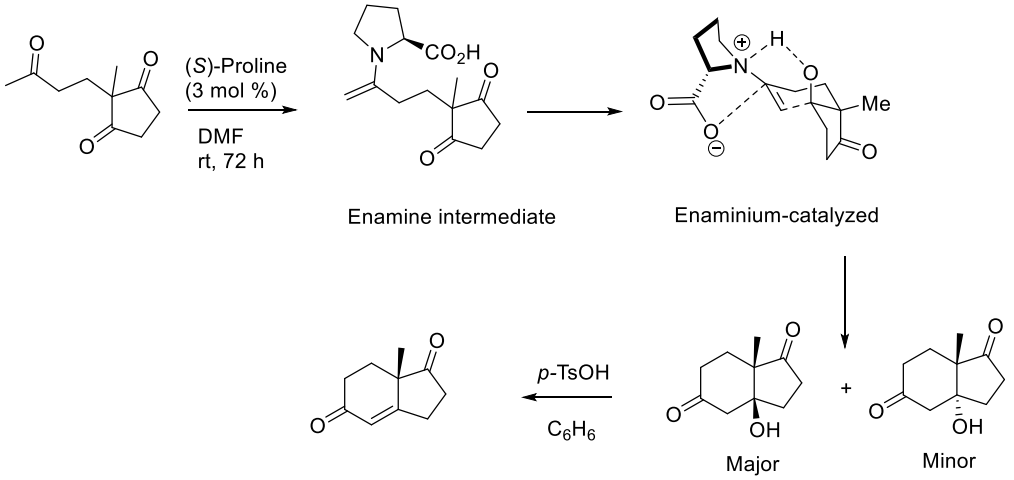
Scheme 2. Hajos-Parrish-Eder-Sauer-Wiechert reaction

This reaction was the first example of a highly enantioselective organocatalytic process. Although its mechanism was not well understood, four main pathways of the C-C bond-forming step have been proposed.[23] Mechanism (A) involves nucleophilic attack by the exocyclic enol to a carbinolamine to displace the catalyst. Acid-catalyzed dehydration of the aldol addition product also gave the condensation product (Scheme 3).



Scheme 3. Proposed mechanism (A) of the Hajos-Parrish-Eder-Sauer-Wiechert reaction

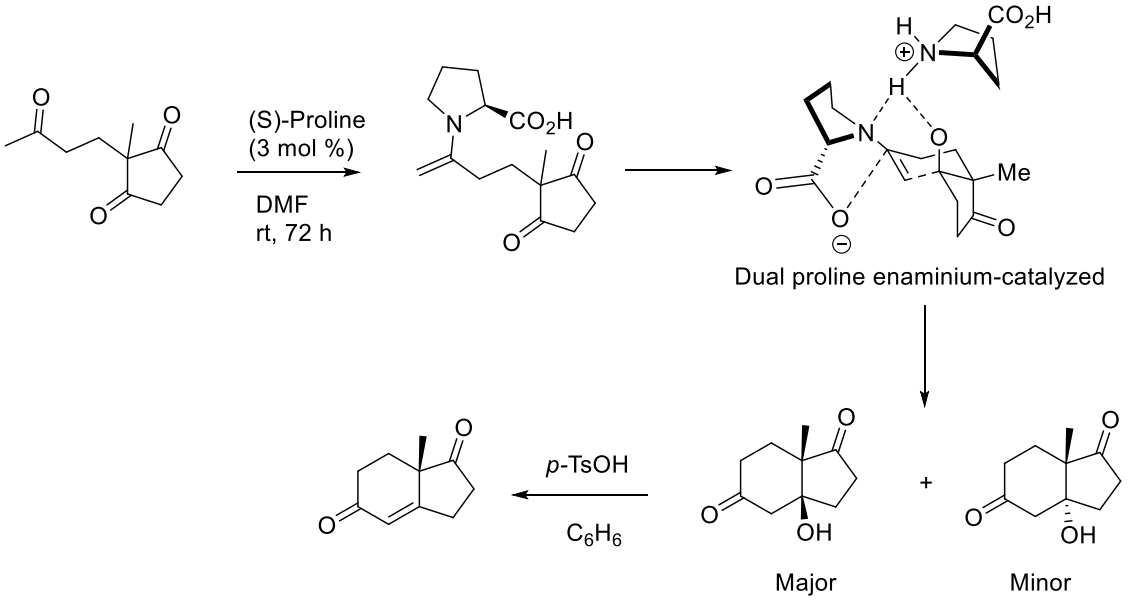
Mechanism (B) involves an enamine intermediate and simultaneous proton transfer following with condensation step (Scheme 4).



Scheme 4. Proposed mechanism (B) of the Hajos-Parrish-Eder-Sauer-Wiechert reaction

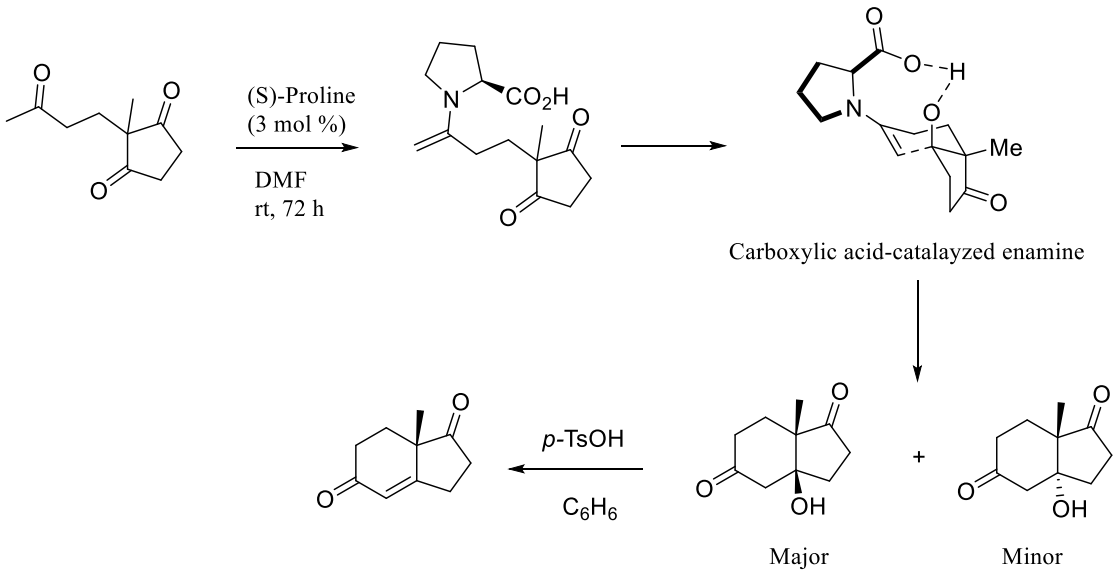
Agami suggested the mechanism (C) and proposed two proline molecules

in the C-C bond forming transition state assisting in the N-H--O hydrogen transfer, based on the small negative nonlinear effect in the asymmetric catalysis[24] (Scheme 5).



Scheme 5. Agami proposed mechanism of the Hajos-Parrish-Eder-Sauer-Wiechert reaction

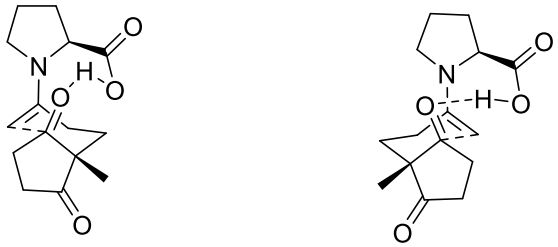
Finally in 1976, Jung proposed a mechanism involving a single molecule of proline and simultaneous proton transfer to the forming alkoxide[25] (Scheme 6).



Scheme 6. Jung proposed mechanism of the Hajos-Parrish-Eder-Sauer-Wiechert reaction

After suggesting the above mechanisms, Houck reported a DFT investigation on all proposed transition states and optimized structures with the B3LYP/6-31G (d) level of theory[26]. He found that the transition state of mechanism A (carbonilamine intermediate) is higher in energy than the uncatalyzed reaction. Also the transition state of mechanism B was found to be about 30 kcal/mol higher in energy than the preferred transition state, due to the distortion of the enamine from planarity. The Agami transition state was also found to be disfavored due to the entropic factor for the presence of another proline molecule. Finally, Houk reported that the mechanism proposed by Jung is favored energetically and about 10 kcal/mol lower than the uncatalyzed process. He argued that this energy difference is because of the enhanced nucleophilicity of the planar enamine as well as the increase of the electrophilicity of the carbonyl by the carboxylic acid. In order to rationalize the stereoselectivity of the Hajos-Parrish-Eder-Sauer-Wiechert reaction product, Houk also investigated the two possible chair Zimmerman-Traxler-like transition states, using the B3LYP/6-31G (d) level of theory[27]. As illustrated in scheme 7,

there are two possible chair Zimmerman-Traxler-like transition states based on the orientation of the enamine with respect to the carboxylic acid. According to the Houk-List model and DFT calculations, the *anti*-transition state leading to main product is 3.4 kcal/mol energetically favored whereas *syn* transition states leads to the formation of the minor product.



anti-TS *syn*-TS

Scheme 7. *anti* and *syn* transition structures of proline catalyzed Hajos-Parrish-Eder-Sauer-Wiechert reaction

The enantioselectivity of the Hajos-Parrish-Eder-Sauer-Wiechert reaction is dependent on two factors. First, the capacity of each of the transition states to achieve the best enamine nucleophilicity. Second, the capacity to achieve the most electrostatic stabilization to the developing negative charge on the carbonyl electrophile. On the one hand, the H of the carboxylic acid group of proline is being transferred to the forming alkoxide, on the other hand there is also a stabilizing hydrogen interaction between the partial positive hydrogen of the carbon adjacent to the proline nitrogen and the forming alkoxide (NCH---O). Based on the above factors, the transition state containing a planar enamine can achieve the best enamine nucleophilicity and also stabilize the forming alkoxide by the NCH---O electrostatic interaction. The enamine of the *syn* TS suffers from distortion, because of the hydrogen transfer to the more proximal alkoxide whereas the enamine of the *anti* TS

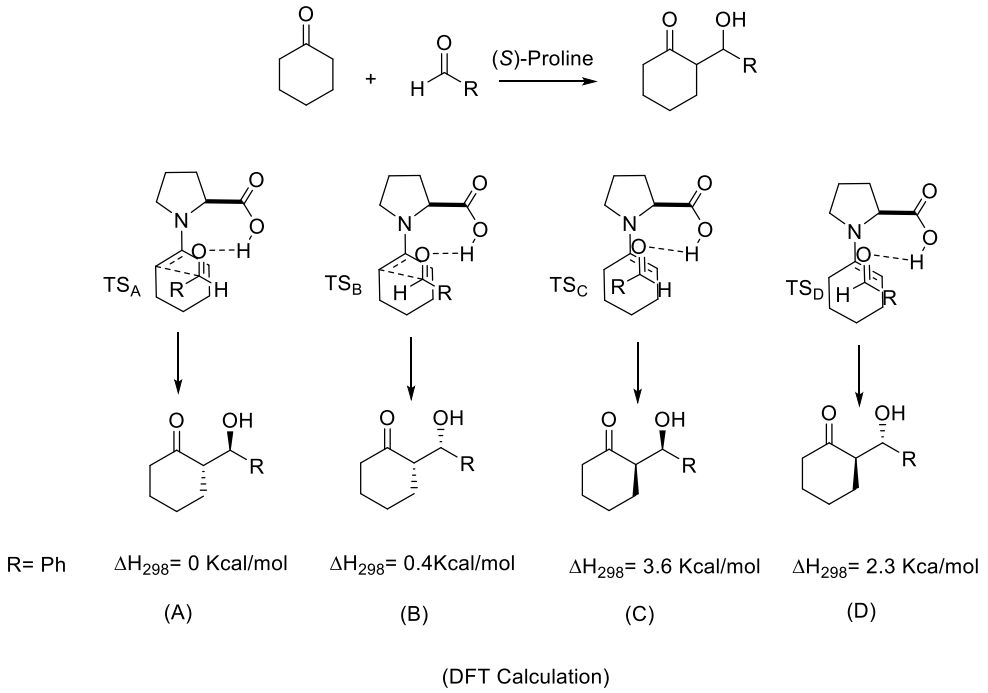
is much more planar. Hence the NCH---O distance in *anti* TS is shorter and the stabilizing hydrogen bonding interaction is greater than *syn* TS.

2-2-1 Houk-List model

The proline-catalyzed aldol reaction of cyclohexanone with aldehydes can produce different stereoisomers. As it is shown in scheme 8, all those stereoisomers are *syn*- and *anti*-diastereomeric pairs of enantiomers. Charge stabilization and C-C bond formation in the transition state could be facilitated by proton transfer from the amine or carboxylic acid group of proline to the forming alkoxide. Therefore, Houk and List only considered the transition states that involve hydrogen bonding between the carboxylate and the aldehyde. As illustrated in scheme 8, the lower energy transition states belong to TS_A and TS_B involving the re attack on the *anti*-enamine, while transition states involving si attack on the *syn*- enamine are higher in energy. The TS_A and TS_B are lower in energy because of the stabilizing hydrogen bond interaction between the partial positive hydrogen of the carbon adjacent to the proline nitrogen to the forming alkoxide. The NCH---O distance in TS_A and TS_B is 2.46 A° and 2.37 A° respectively. On the other hand, transition states involving the *syn* enamine (TSC and TS_D) have larger NCH---O distances (3.12 A° and 3.18 $A^{\circ)}$ and as a result the electrostatic stabilization of these transition states is diminished. Moreover, considering the reaction between benzaldehyde and cyclohexanone in Scheme 8, TS_B is slightly higher in energy than TS_A because of the additional interaction of the phenyl ring of the aldehyde with the cyclohexane enamine.

According to the Houk-List model and based on computational studies and DFT calculations of the proline catalyzed reaction of cyclo hexanone and aldehydes, the

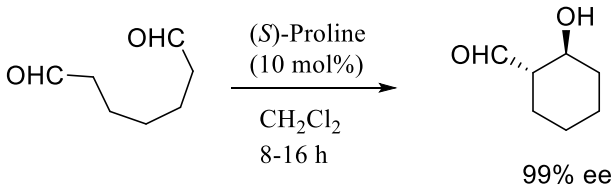
transition states involving the re attack on the *anti*-enamine has the lowest energy and leads to the *anti* aldol product (structure A in the Scheme 8)[28].



Scheme 8. Relative energies of transition states for the reaction of *syn*- and *anti*-enamine with benzaldehyde

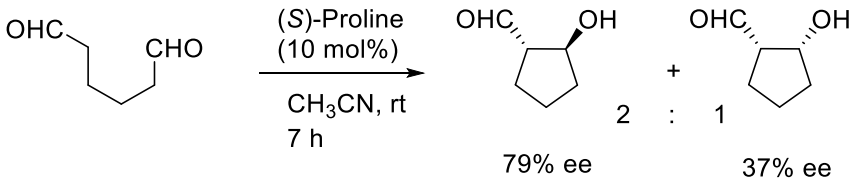
2-3 Enolexo Intramolecular Aldolizations

The first catalytic asymmetric enolexo intramolecular aldolization was reported by List in 2003.[29] The reaction of heptanedial with a catalytic amount of (*S*)-proline in the presence of dichloromethane, gave highly enantioselective enolexo aldolization of dicarbonyl compounds (Scheme 9).



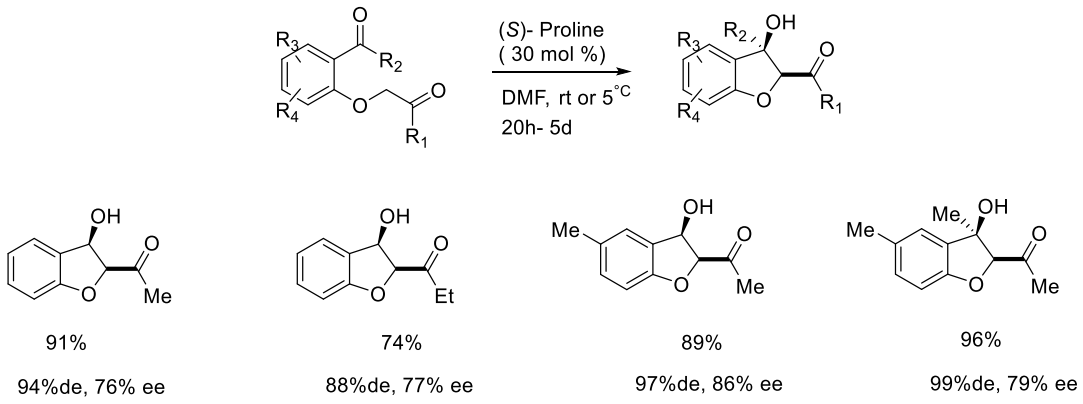
Scheme 9. Proline-catalyzed 6-*enolexo* aldolization.

Although proline-catalyzed 6-*enolexo* aldolization led to high stereoselectivity, 5-*enolexo* aldolizations gave modest diastereo- and enantioselectivities[30] (Scheme 10).



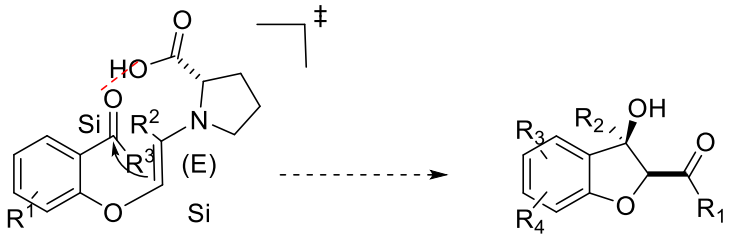
Scheme 10. Proline-catalyzed 5-*enolexo* aldolization

Three years later, Enders and co-workers reported the synthesis of dihydrobenzofuranol as a class of natural products, through an asymmetric intramolecular *cis* 5-enolexo aldolization of dicarbonyl compounds[31] (Scheme 11).



Scheme 11. Proline-Catalyzed asymmetric 5-enolexo aldolization of dicarbonyl compounds

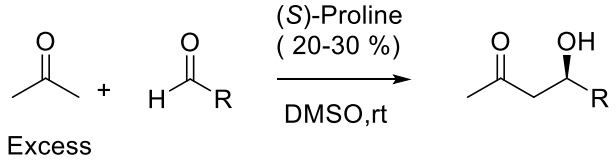
Once again, (*S*)- proline was found to be a productive catalyst and final products were produced in moderate to high diastereoselectivities and good enantioselectivities in the presence of 0.1 M DMF as solvent and under re-crystallization from an *n*-hexane/EtOAc mixture. The stereoselectivity of the asymmetric organocatalytic intramolecular 5-*enolexo* aldol reaction can also be rationalized by the Houk–List-type transition-state model shown in Scheme 12.

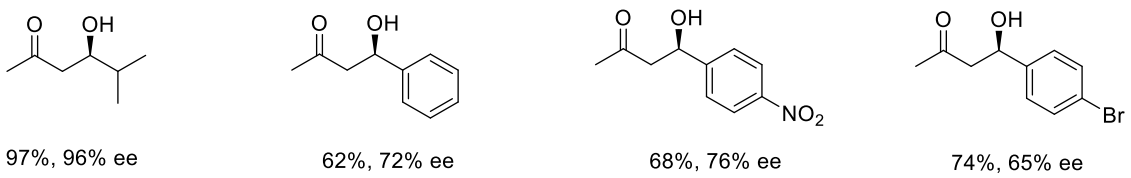


Scheme 12. Transition state of 5-*enolexo* aldol reaction

2-4 Intermolecular Aldolizations

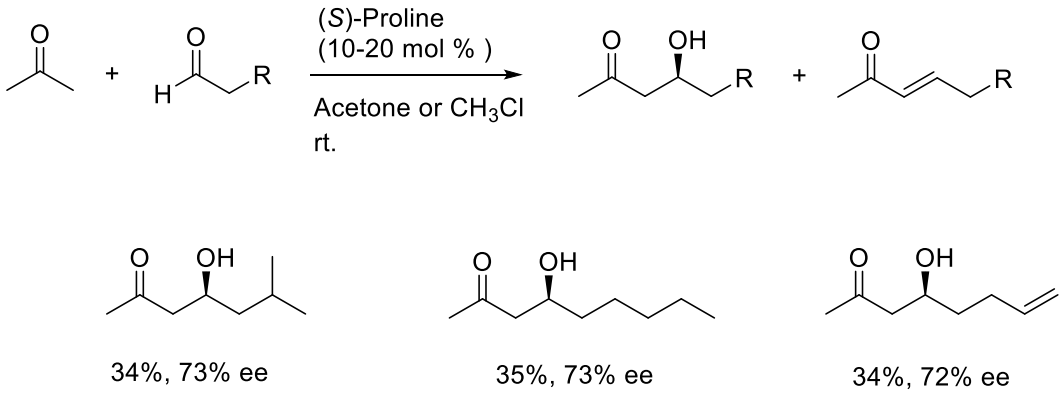
The first intermolecular proline-catalyzed aldolization was reported by List in 2000[32]. Based on these investigations[33,34], aldol products can be produced with good yields and enantioselectivities in the reaction of excess acetone with some aromatic and α-branched aldehydes in the presence of (*S*)- proline as a catalyst (20-30 mol %) and DMSO as a solvent (Scheme 13).





Scheme 13. Proline-catalyzed direct asymmetric intermolecular aldol reaction.

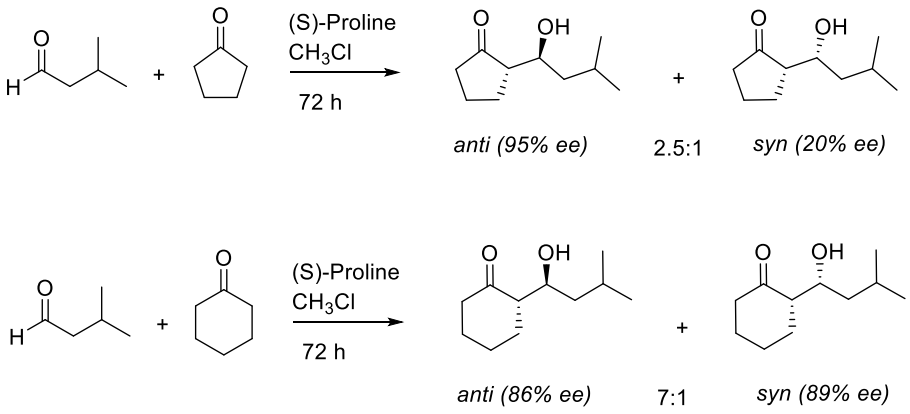
Unlike α-branched aldehydes, for α-unbranched aldehydes, homo-aldol addition and condensation of the aldehyde or elimination reaction of the aldol product are the main side reactions in the presence of DMSO. By using acetone or acetone/chloroform mixtures instead of DMSO as the solvent, and 10-20 mol % proline as the catalyst, the cross-aldol product could be isolated with acceptable yield and enantioselectivity from the other unwanted products (Scheme 14).



Scheme 14. Proline-catalyzed aldol reactions of acetone with α-unbranched aldehydes

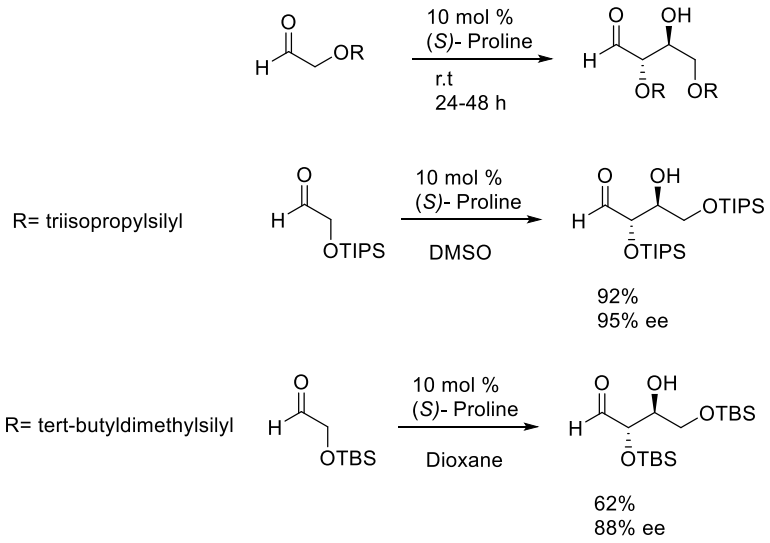
Cyclic ketones also can be used in proline-catalyzed intermolecular aldolizations .The stereoselectivity of the main product is in accordance with the Houk-List model. For

instance, cyclopentanone reacted with isovaleraldehyde in chloroform and produced a 2.5: 1 mixture of *anti* and *syn* diastereomers with 55% and 22% yield respectively. Cyclohexanone reacted with isovaleraldehyde in chloroform and produced 7:1 mixture of *anti* and *syn* diastereomers in 41% yield. Also the main isomer was formed in 86% ee and the minor isomer was formed in 89% ee (Scheme 15).



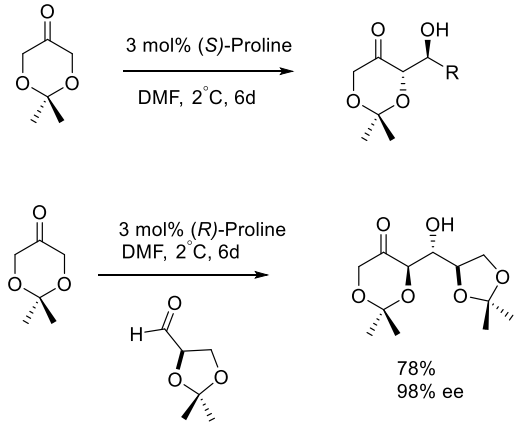
Scheme 15. Aldol reactions of cyclic ketones.

Enders and MacMillan[35] have also reported that, in a transformation such as the aldol reaction (especially those involving dihydroxy acetone derivatives), chiral amines played an important role and can catalyze the reaction giving excellent enantioselectivity. Based on MacMillan's investigations, the direct enantioselective catalytic aldol reaction using α-oxygenated aldehydes can be catalyzed with (*S*)-proline with acceptable levels of enantiocontrol and reaction efficiency in the presence of electron-rich oxyalkyl substrates (Scheme 16).



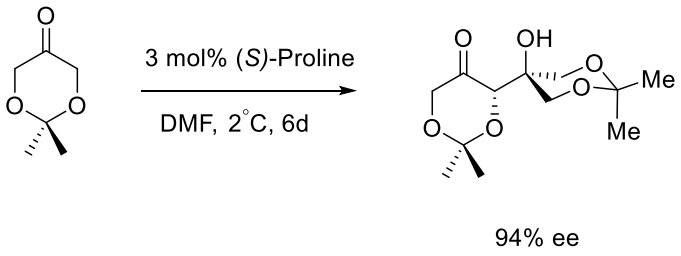
Scheme 16. Organocatalytic aldol dimerization of α-oxyaldehydes.

However, Enders and Grondal[36] applied the aldol reaction as a key step in the synthesis of carbohydrates by using dioxanone and various aldehydes and (*S*) - and (*R*)-proline as a catalyst. When the reaction was carried out with suitable aldehydes in the presence of 30 mol % proline in DMF at 2 °C, *anti*-aldol products were obtained, in accordance with the Houk-List model, with moderate to good yields and excellent diastereo- and enantioselectivities (Scheme 17).



Scheme 17. Proline-Catalyzed asymmetric aldol reaction of dioxanone with aldehyde.

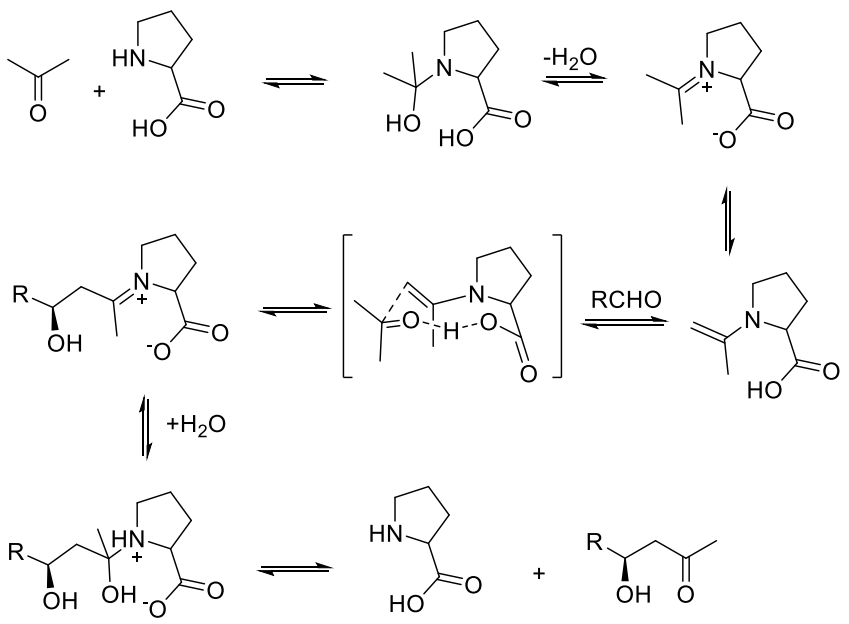
It should also be noted that, by using dioxanone as a substrate in the proline-catalyzed intermolecular aldolization process, self-aldolization is possible with 94% ee, but only in moderate yields (57%)[25] (Scheme 18).



Scheme 18. (*S*)-proline-catalyzed asymmetric self-aldol condensation

2-5 Mechanism of the Proline-Catalyzed Aldol Reaction

Primary amino acids are poor catalysts for the intermolecular aldol reaction[37]. Moreover, carboxylate plays an important role in the enamine mechanism which explains why prolinamide is an inferior catalyst compared to proline in terms of both activity and enantioselectivity. The proposed mechanism of the proline-catalyzed aldol reaction begins with the nucleophilic attack of the amino group. The next step is dehydration of the carbinol amine intermediate and then deprotonation of the iminium species. In the presence of aldehyde, the carbon-carbon bond forming step occurs through a Zimmermann-Traxler-type transition state. Finally both steps of the hydrolysis of the iminium-aldol intermediate take place to provide the anti-aldol product (Scheme 19).

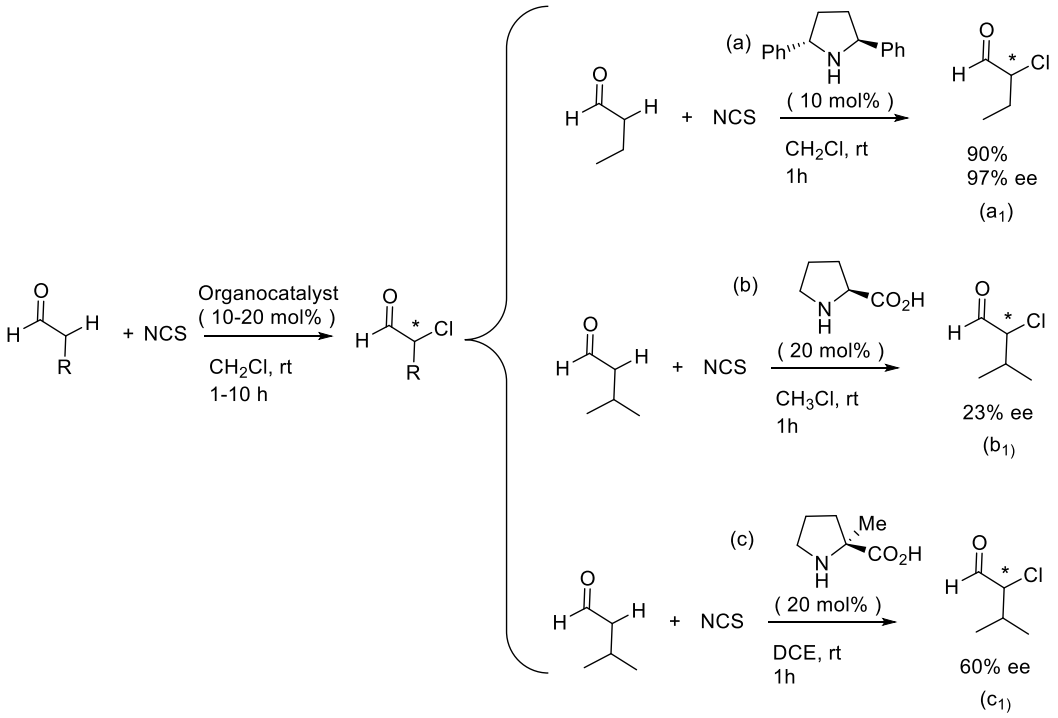


Scheme 19. Proposed mechanism of the proline-catalyzed asymmetric aldol reaction.

2-6 Organocatalytic asymmetric α-chlorination of aldehydes

Optically active halogen-containing compounds play a significant role as synthetic intermediates[38]. Producing α -chloro aldehydes as building blocks for natural product synthesis with excellent yield and enantioselectivities is one of the crucial targets for organic chemists. Based on the Jorgensen protocol[39] (Scheme 20), N-chlorosuccinimide (NCS) is an inexpensive and excellent chlorine source for producing α -chloro aldehydes with acceptable yield and enantioselectivity. Even though the chiral amine (a) catalyzes the α-chlorination of butyraldehyde with good yield and enantioselectivity, 2-chloro-3-methylbutanal (b_1) was found with only 23% ee using proline as a catalyst. According to the Jorgensen protocol, both the yield and optical purity are dependent on the solvent. For

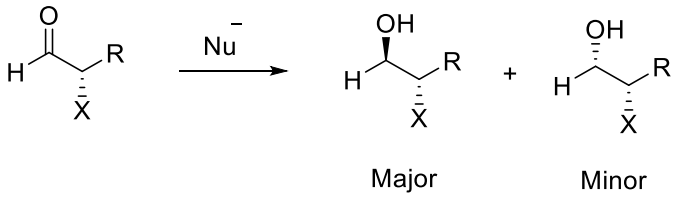
instance, by using 2-methyl-(*S*)-proline instead of proline as the catalyst and 1,2-dichloroethane (DCE) as the solvent, the enantioselectivity improved significantly.



Scheme 20. Jorgensen organocatalytic asymmetric α-chlorination of aldehydes.

2-7 Nucleophilic addition to α-heteroatom-substituted aldehydes

Designing of any effective synthesis requires consideration of the stereochemistry of the product. Hence the ability to accurately predict the stereochemistry in the addition of a nucleophile to an aldehyde bearing an adjacent α-heteroatom substituent is essential (Scheme 21). After testing different models to predict 1,2-induction in nucleophilic addition to α-heteroatom-substituted aldehydes, the polar Felkin-Anh model and Evans-Cornforth models have been found to be the most efficient[40]. In both models, addition of a nucleophile to an aldehyde bearing an adjacent α-heteroatom substituent leads to the *anti* diastereomer as the main product.

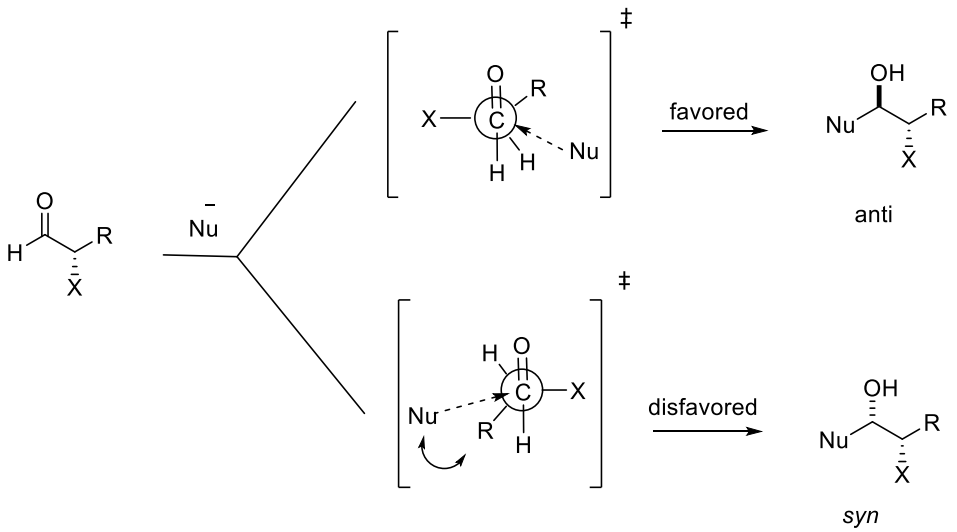


Scheme 21. Nucleophilic addition to α-heteroatom-substituted aldehydes

2-7-1 The polar Felkin-Anh model

The polar Felkin-Anhh model was initially proposed by Felkin[41] and then revised by Anh and Eisenste[42]. Felkin first argued that previous models did not take torsional strain into account in partially formed bonds in the transition state. He then proposed that a staggered transition state would be more beneficial than an eclipsed transition state. He argued that torsional strain represents a significant fraction of the strain between fully formed bonds and thus proposed the first fully staggered transition state model. Anh and Eisenstein later added the Bürgi- Dunitz attack angle regarding the route of nucleophilic attack on carbonyls. They also provided a logical explanation for the polar effect that specifies a perpendicular alignment between the polar α-substituent and the carbonyl moiety. Based on the Polar Felkin-Anh model, there is a hyperconjugative interaction of the forming bond (*HOMO*) with the best vicinal acceptor, the C-X bond (*LUMO*). The hyperconjugative interaction will be maximized when the forming bond and the C-X bond are antiperiplanar (Scheme 22). As it is illustrated in Scheme 22, the two transition states are distinguished by steric interactions between the nucleophile and α-substituents. In the favored transition state, the nucleophile approaches a hydrogen atom whereas the

disfavored transition state is destabilized by the steric interaction between the nucleophile and the alkyl substituent.

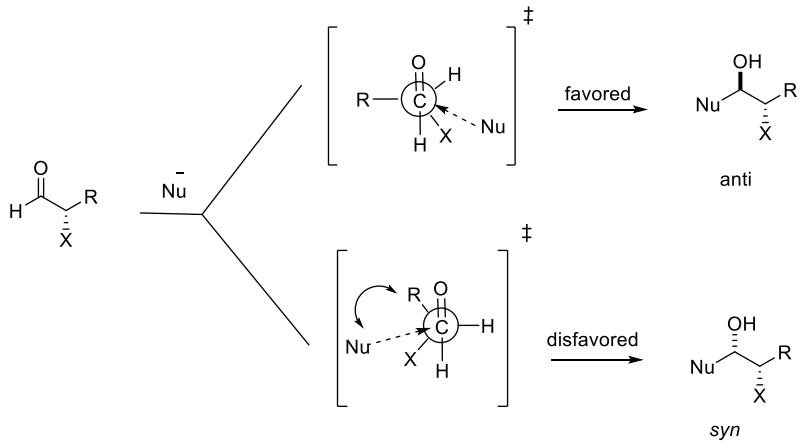


Scheme 22. The Polar Felkin-Anh model.

2-7-2 The Evans-Cornforth model

In 1959 Cornfoth[43] proposed the first version of this model which was later modified by Evans[44] in 2003. Cornforth suggested that in nucleophilic additions to α-heteroatom substituted carbonyl compounds, minimization of the dipole moment is a key element for determining the transition state energy and stereochemistry of the product. Based on the Evans-Cornforth model, dipole minimization between the C-X bond and the adjacent carbonyl group takes place while the relationship between them is antiparallel dihedral angle. As depicted in Scheme 23, in both transition states having the electronegative substituent and carbonyl group, a dipole-minimized orientation caused the antiparallel dihedral angle relationship between the carbonyl and the α-X substituent. Like the Polar

Felkin-Anh model, the two relevant transition states can be further distinguished by steric interaction. In the favored transition state leading to the *anti*-product, the nucleophile approaches between the heteroatom substituent and a hydrogen atom whereas the disfavored transition state is destabilized because of the steric interaction between the nucleophile and the alkyl substituent.

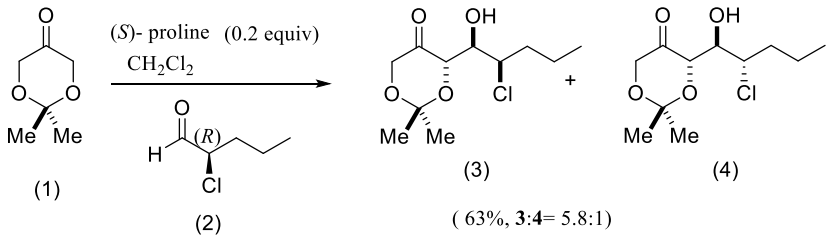


Scheme 23. The Evans-Cornforth model.

2-8 Results and discussion

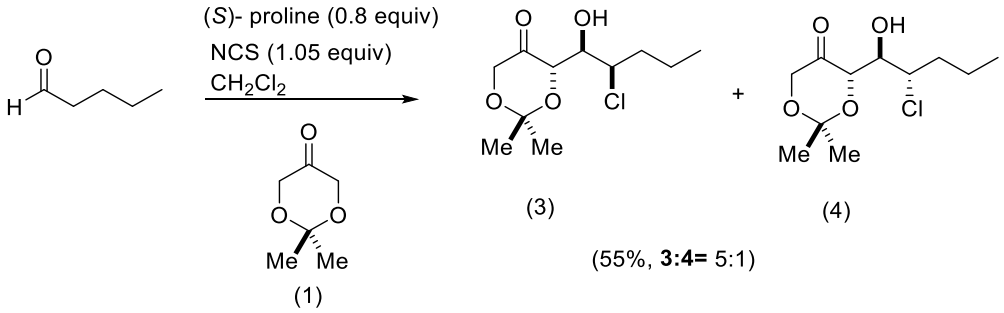
2-8-1 (*S*)-Proline catalyzed reaction of 2, 2-dimethyl-1, 3-dioxan-5- one and 2-chloro pentanal.

The Britton research group investigated the *(S)*-proline catalyzed aldol reaction in the presence of 2,2-dimethyl-1,3-dioxan-5-one (1) with (*R*)-2-chloropentanal prepared by the Jorgensen[39] protocol. Based on this aldol reaction, the *syn*-chlorohydrin product was preferred over *anti*- chlorohydrin product with 63% yield and ca. 6:1 mixtures of diastereomers (Scheme 24).



Scheme 24. Diastreoselectivity in a one pot, two step procedure for a proline-catalyzed aldol reaction.

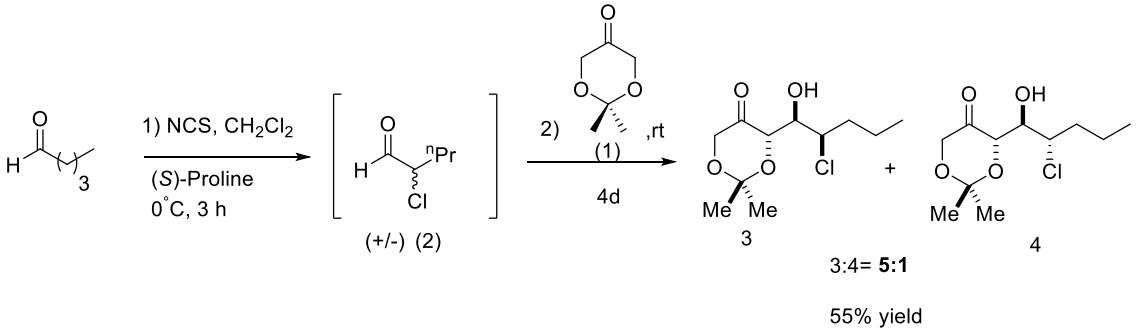
This reaction entails two different steps; first chlorination of the aldehyde in accordance with the Jorgensen protocol and then a one-pot *(S)*-proline-catalyzed aldol reaction between the dioxanone and the chlorinated aldehyde. Alternatively, a one-pot, one-step reaction can take place by adding all of the reagents at once. The *syn*-chlorohydrin *anti* aldol adduct is produced diastereoselectivity in good yield in both cases (Scheme 25).



Scheme 25. One-pot, one-step procedure of proline-catalyzed aldol reaction.

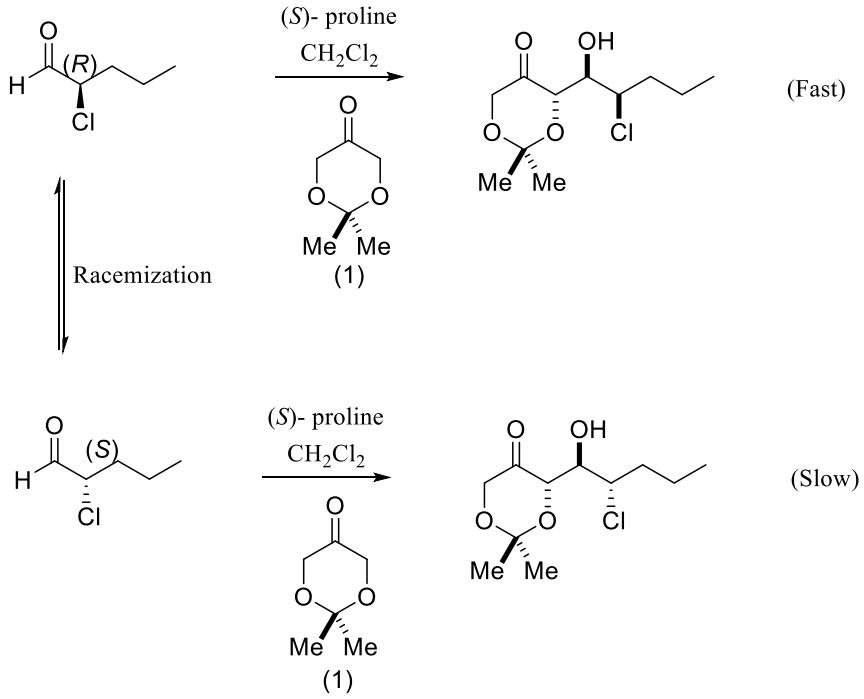
2-8-2 Dynamic kinetic resolution (DKR) in the proline-catalyzed aldol reaction

In the (*S*)-proline catalyzed chlorination of pentanal in the presence of NCS (Scheme 26), both (*R*)-2-chloropentanal and (*S*)-2-chloropentanal were produced as intermediates.



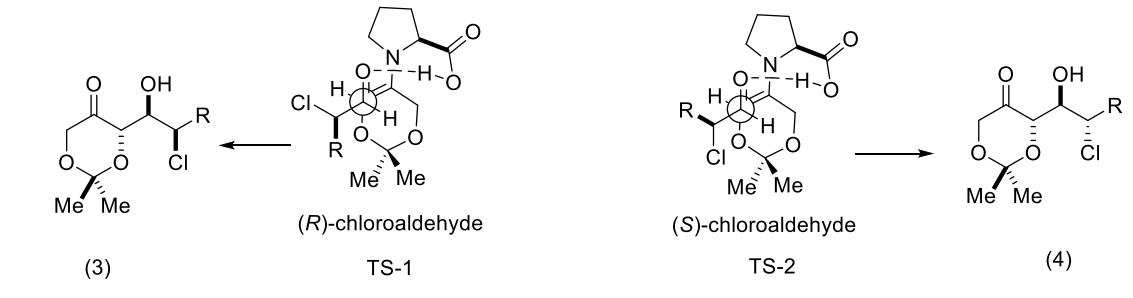
Scheme 26. Generating both (*R*)-2-chloropentanal and (*S*)-2-chloropentanal in the (*S*)-proline catalyzed chlorination of pentanal with NCS.

Syn-chlorohydrin is then generated diastereotopically in good yield by *Dynamic Kinetic Resolution* (DKR) [45] of the proline-catalyzed aldol reaction between dioxanone (1) and (*R*)-2-chloropentanal (Scheme 27).



Scheme 27. Dynamic kinetic resolution (DKR) proline-catalyzed aldol reaction.

Optimized different transition states and a comparison of their structures (which will be explained in parts 3-3, 3-4 and 3-5) revealed a potential explanation for the preferential (*R*)-chloroaldehyde intermediates involving an avoidance of steric interactions as well as destabilizing electrostatic interactions (Scheme 28).



Scheme 28. Potential transition structures leading to aldol adducts 3 and 4.

Since the experimentally synthesized product data is also available to validate the theoretical results, the wB97xd[46] /6-31G (d) [47] level of theory, which includes empirical dispersion and designed to provide long-range correlation[48,] was applied and relative the difference in energy of the optimizing structures were calculated. The wB97XD functional can better treat hydrogen bonding and van der Waals interactions than conventional DFT.[6]

2-8-3 Comparing relative free energy of different transition state structures of the reaction between enamine fragment and α-chloro pentanal

Following our collaborative computational work with the Britton group, we first investigated different geometries of transition states in the reaction between the *R* and *S* α-chloropentanal and enamine fragments (The enamine fragment was generated from the reaction between (*S*)-proline and dioxanone) (Scheme 25 and 28). Although *anti*-aldol products are rationalized based on the Houk-List model, the observed *syn*-chlorohydrin selectivity (Figure 1-C) is not in accordance with the polar Felkin-Anh (Figure 1-A) or the Evans-Cornforth models (Figure 1-B). After optimizing all of the transition states, computational calculations revealed that, transition structure C (Dudding-Britton model) is the lowest in energy and the preferred transition structure leading to the *syn*-chlorohydrin product. On the other hand, both transition states A and B, which are in accordance with the polar Felkin-Anh and Evans-Cornforth models respectively, led to *anti*-chlorohydrin products (Figure 1). The energy differences of the transition structures for a given reaction can be understood by a closer analysis of their geometries based on steric and electrostatic factors.

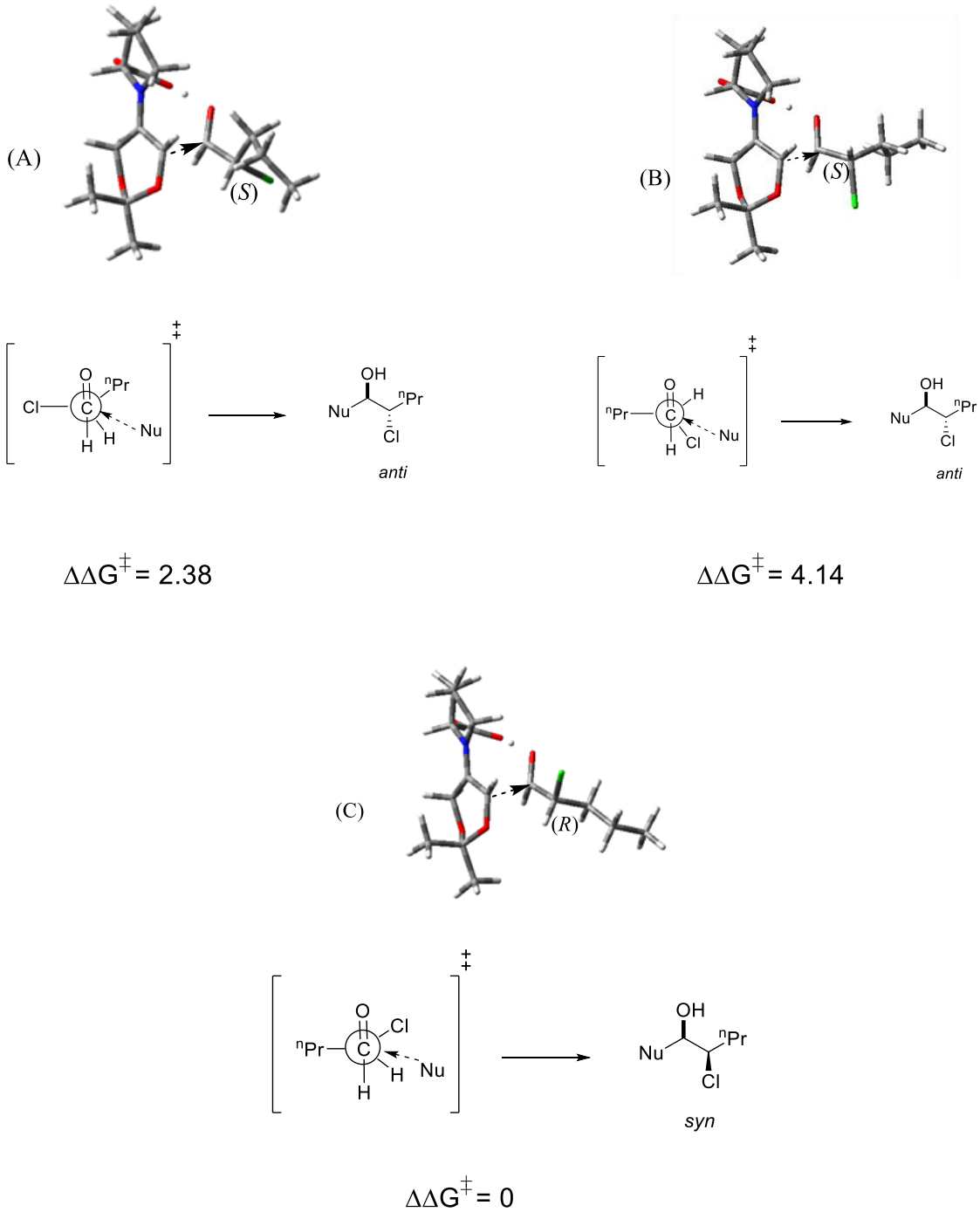
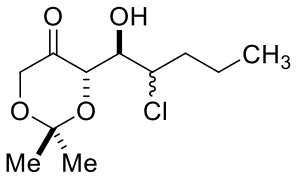
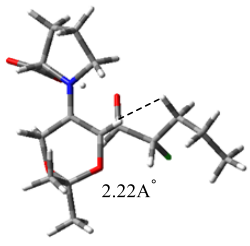


Figure 1. Relative free energies (kcal/mol) of different transition state structures for proline-catalyzed α-chlorination/aldol reaction between enamine fragment and chloro pentanal based on: A) The polar Felkin-Anh model B) The Evans-Cornforth model and C) The Dudding-Britton model.

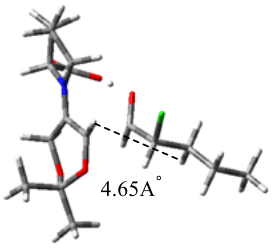
2-8-4 Steric destabilizing interaction in the polar Felkin-Anh model

In order to rationalize why the Dudding-Britton model is the favored transition structure of the alodol reaction between the enamine and different aldehydes, leading to *syn*-chlorohydrin selectivity, we compared this model with both the polar Felkin-Anh and Evans-Cornforth models and considered both the steric and electrostatic factors between the favored and disfavored models. Our computational studies showed that there is a destabilizing steric interaction between H2 of the enamine fragment with the β-hydrogen of the aldehyde in all of the (*S*)-chloroaldehyde intermediates based on the Polar Felkin-Anh model (Figure 2), whereas such a destabilizing interaction does not exist in the (*R*)-chloroaldehyde counterparts based on the Dudding-Britton model. For instance, while the distance between H2 of the enamine and the β-hydrogen of (*R*)-2-chloropentanal in the favored Dudding-Britton transition model is 4.65 A°, this distance becomes shorter to 2.22 A° between the β-hydrogen of (*S*)-2-chloropentanal and H2 of the enamine fragment in the disfavored polar- Felkin-Anh transition model.



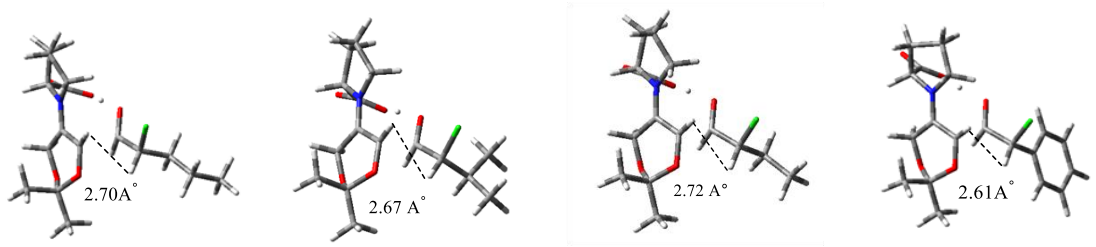


(*S*)-2-chloropentanal
(*Polar Felkin-Anh model*)

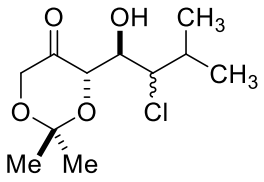


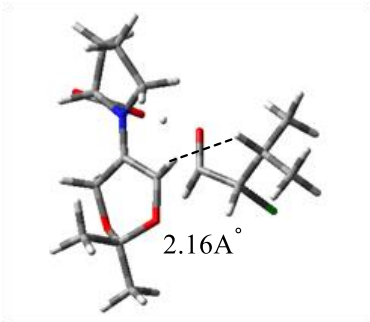
(*R*)-2-chloropentanal
(*Dudding-Britton model*)

It should also be noted that, there is no destabilizing steric interaction between H2 of the enamine and the α-hydrogen of the aldehyde in all Dudding-Britton transition models.

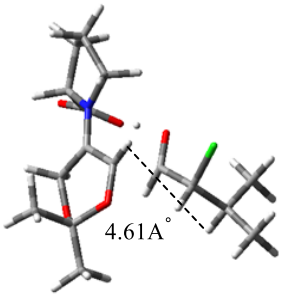


Because of the ample distance between H2 of the enamine fragment and the β-hydrogen of (*R*)- iso-propyl chloroaldehyde in the Dudding-Britton transition state model, there is no destabilizing steric interaction. Hence, this model is more favorable than the transition state based on the Polar Felkin-Anh model. (As depicted in figure 2, the distance between H2 of the enamine fragment and the β-hydrogen of (*S*) - iso-propyl chloroaldehyde based on the Polar Felkin-Anh transition model is 2.16 A°).

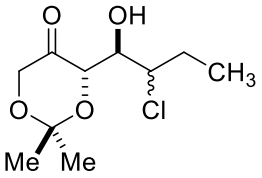


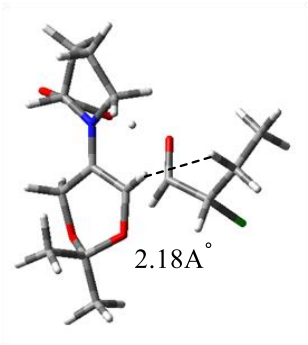


(*S*)- Iso-propyl chloroaldehyde
(*Polar Felkin-Anh model*)

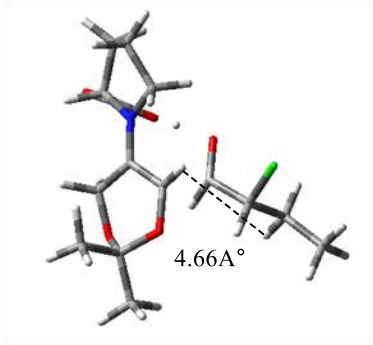


(*R*)- iso-propyl chloroaldehyde
(*Dudding-Britton model*)

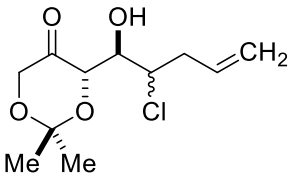


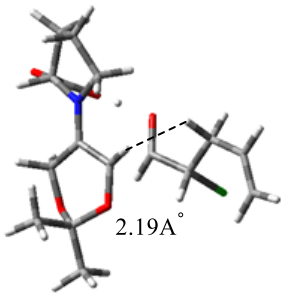


(*S*)- 2-chlorobutanal
(*Polar Felkin-Anh model*)

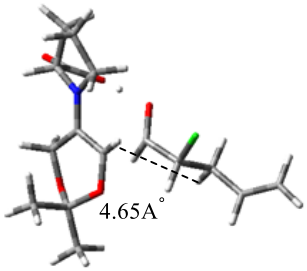


(*R*)- 2-chlorobutanal
(*Dudding-Britton model*)





(*S*)-2-chloropent-4-enal
(Felkin-Anh model)



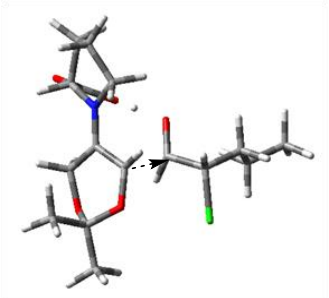
(*R*)-2-chloropent-4-enal
(*Dudding-Britton model*)

Figure 2. Destabilizing steric interaction between the H2 of the enamine with the β-hydrogen of the aldehyde in the polar Felkin-Anh model.

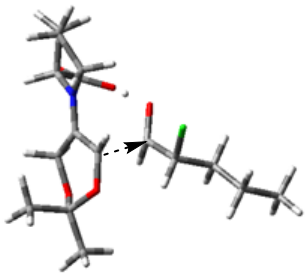
2-8-5 Destabilizing electrostatic interaction in the Evans-Cornforth model

As shown in figure 1, computational studies of the different possible transition states between *R* and *S* α-chloropentanal and the enamine fragment, revealed that the Evans-Cornforth transition state model (Figure 1B) is 4.14 kcal/mol higher in energy than the Dudding-Britton model (Figure 1C) and leads to the *anti*-chlorohydrin product.

(B)



(C)



$\Delta\Delta G^{\ddagger} = 4.14$ $\Delta\Delta G^{\ddagger} = 0$

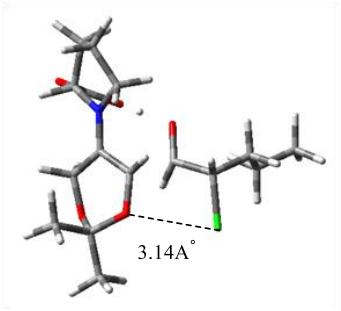
According to the Evans-Cornforth model (Scheme 23), dipole minimization between the C-X bond and the adjacent carbonyl group takes place while the relationship between them is antiparallel dihedral angle. Thus, there should be a destabilizing electrostatic interaction between the Cl and O atoms in (*S*)-chloroaldehyde in the Evans-Cornforth model. The atoms-in-molecules (AIM) method[49] confirms this (Figure 3). AIM theory has proved to be a valuable tool to understand the concept of a chemical bond and its strength in terms of electron density distribution. According to AIM data (Table 1), while the charge density (ρ) is small, the positive value of Laplacian ($\nabla^2\rho$) indicates a typical closed-shell, mostly electrostatic interaction.[50,51] In other words, a negative Laplacian at the bond critical point (BCP) stands for all shared-electron (covalent) interactions while in all closed-shell (electrostatic) interactions there is a positive Laplacian at the bond critical point.

Table 1

The wB97xd/6-31G (d) calculated bond critical point (BCP) data.

Bond	ρ	$\nabla^2\rho$
O—Cl	0.009	0.035

(B)



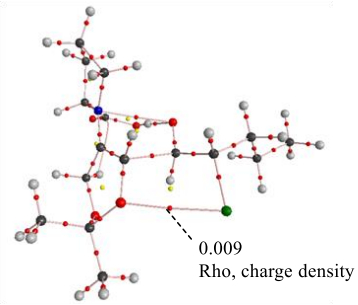


Figure 3. Destabilizing electrostatic interactions existing between the Cl and O atom in Evans-Cornforth transition model between (*S*)-2-chloro pentanal and enamine fragment.

It should also be noted that, the total electron energy density (H_b) at the bond critical point is a more appropriate index to provide a better understanding of the nature of interactions between atoms[52]. There is a relation between total electron energy density (H_b) and kinetic (G_b) plus potential (V_b) energy density (equation 1). Moreover, there is a relation between the Laplacian and the components of the total energy density (H_b) (equation 2).

$$H_b = G_b + V_b \qquad (1).$$

$$1/4\nabla^2_{\rho b} = 2G_b + V_b \qquad (2).$$

G_b is a positive value, whereas V_b is a negative one. The sign of H_b at bond critical point determines whether the interaction is electrostatic dominant (H > 0) or covalent dominant (H < 0). The Laplacian is negative if the absolute value of the potential energy is bigger than two times the kinetic energy, which implies the covalent character of interaction, like covalent bonds and very strong hydrogen bonds. Moreover, while H_b is positive, the

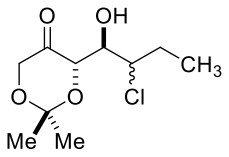
low and positive $\nabla^2{}_{\rho b}$ at the BCP indicates the typical of closed-shell interactions (Table 2).

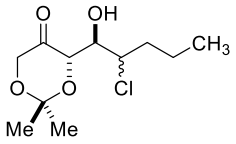
Table 2

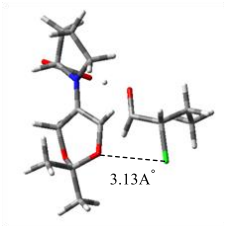
The charge electron density(ρ), the Laplacian ($\nabla^2\rho$), kinetic energy density ($G_{(b)}$), potential energy density($V_{(b)}$) and the total electronic energy density (H_b) at the bond critical point (BCP) .

Bond	ρ	$\nabla^2\rho$	G_b	V_b	H_b
O—Cl	0.009	0.035	0.0080	-0.0071	0.0009

As illustrated in Figure 4, in the optimized Evans-Cornforth model transition state between the (*S*)-2-chlorobutanal and the enamine fragment (Figure 4, A), the distance between Cl and O atoms is the same as it is between the enamine and the (*S*)-chloropentanal (Figure 4, B). As a result, the difference relative free energies (kcal/mol) between the favored Dudding-Britton model and the disfavored Evans-Cornforth model is the almost same. On the other hand, the Cl and O atoms are closer in the optimized Evans-Cornforth transition state model between the (*S*)-2-chloro-2-phenylacetaldehyde and the enamine (Figure 4,C). Hence, the relative free energy (kcal/mol) between the favored Dudding-Britton model and the disfavored Evans-Cornforth model becomes greater to 6.09 kcal/mol.

A) 

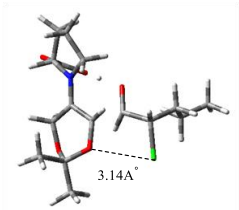
B) 



$\Delta\Delta G^{\ddagger} = 4.49$

(*S*)-2-chlorobutanal

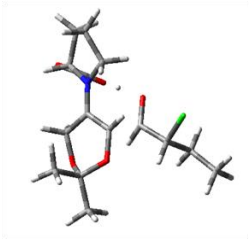
(Evans-Cornforth model)



$\Delta\Delta G^{\ddagger} = 4.14$

(*S*)-2-chloropentana

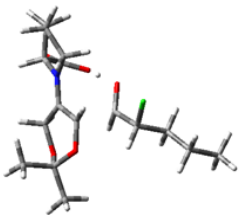
(Evans-Cornforth model)



$\Delta\Delta G^{\ddagger} = 0$

(*R*)-2-chlorobutanal

(Dudding-Britton model)

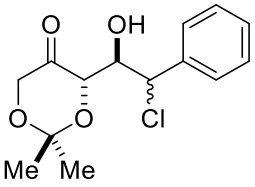


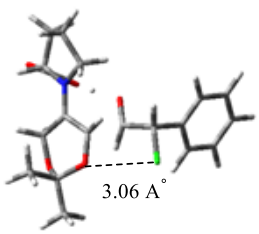
$\Delta\Delta G^{\ddagger} = 0$

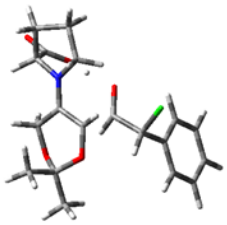
(*R*)-2-chloropentanal

(Dudding-Britton model)

C)







$\Delta\Delta G^{\ddagger} = 6.09$

(*S*)-2-chloro-2-phenylacetaldehyde
(Evans-Cornforth model)

$\Delta\Delta G^{\ddagger} = 0$

(*R*)-2-chloro-2-phenylacetaldehyde
(Dudding-Britton model)

Figure 4. The relative free energies (kcal/mol) of transition state between the enamine and aldehyde in (A): 2-chlorobutanal (B): 2-chloropentanal and (C): 2-chloro-2 phenylacetaldehyde based on Evans-Cornforth model and Dudding-Britton model.

AIM data also showed a small charge density and a positive value for the Laplacian ($\nabla^2\rho$) as well as positive value of total electron energy density (H_b) for the both Evans-Cornforth model transition states between (*S*)-2-chlorobutanal (Table 3) and (*S*)-2-chloro-2-phenylacetaldehyde (Table 4) with the enamine intermediate (Figure 5).

Table 3

The charge electron density(ρ), the Laplacian ($\nabla^2\rho$), kinetic energy density (G_b), potential energy density(V_b) and the total electronic energy density (H_b) at the bond critical point (BCP) .

Bond	ρ	$\nabla^2\rho$	G_b	V_b	H_b
O—Cl	0.01	0.036	0.0080	-0.0072	0.0008

(A)

Table 4

The charge electron density(ρ), the Laplacian ($\nabla^2\rho$), kinetic energy density (G_b), potential energy density(V_b) and the total electronic energy density (H_b) at the bond critical point (BCP) .

Bond	ρ	$\nabla^2\rho$	G_b	V_b	H_b
O—Cl	0.01	0.041	0.0091	-0.0072	0.0019

(B)

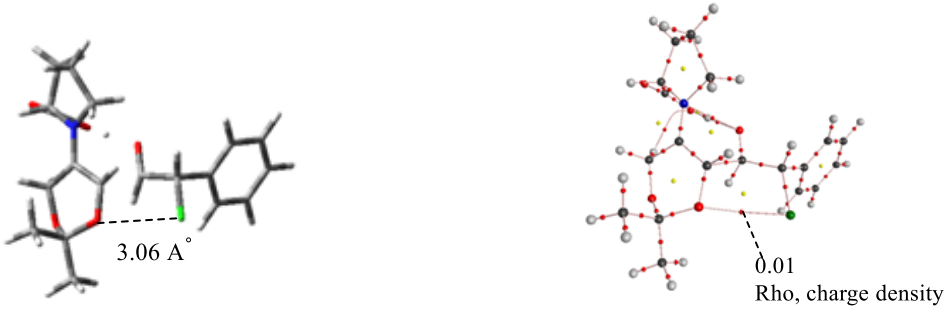


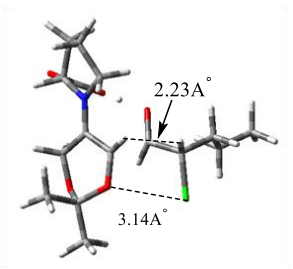
Figure 5. AIM data analysis of transition states between (A): (*S*)-2-chlorobutanal and (B): (*S*)-2-chloro-2-phenylacetaldehyde with the enamine based on the Evans-Cornforth model.

After optimizing different transition states in the aldol reaction of various aldehydes with the (*S*)-proline-derived enamine and by calculating the relative free energies (kcal/mol), it was revealed that the Evans-Cornforth was the least stable model among proposed transition state models (Table 5).

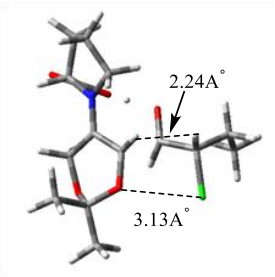
Table 5

	Relative Free energy				
Entry	Aldehyde	*Polar Felkin-Anh (kcal/mol)*	*Evans-Cornforth (kcal/mol)*	*Dudding-Britton (kcal/mol)*	Experimental result diastereomeric ratio
1	Pentanal	2.38	4.14	0	6:1 *syn* over *anti*
2	Butanal	1.75	4.49	0	3.8:1 *syn* over *anti*
3	Phenylacetaldehyde	0.51	6.09	0	2:1 *syn* over *anti*
4	pent-4-enal	1.04	4.16	0	5:1 *syn* over *anti*
5	3-methylbutanal	1	3.22	0	22:1 *syn* over *anti*

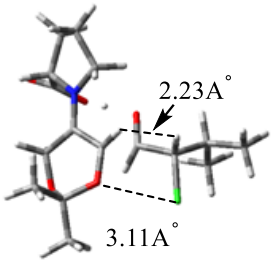
According to Table 5, the Evans-Cornforth models have higher relative free energies in comparison with the both Dudding-Britton and Polar Felkin-Anh models. This fact could be further elaborated by considering both disfavored steric and electrostatic factors in the Evans-Cornforth model at the same time. On the one hand, there is a destabilizing electrostatic interactions between the Cl and O atoms. On the other hand, there is a destabilizing steric interaction between H2 of enamine and α-hydrogen of aldehyde (Figure 6).



(*S*)-2-chloro pentanal



(*S*)-2-chloro butanal



(*S*)- iso-propyl chloroaldehyde

Figure 6. Existing both disfavored steric and electrostatic factors in the Evans-Cornforth transition model of the reaction between different aldehydes and (*S*)-proline-derived enamine

2-8-6 Stabilizing electrostatic interaction in the Dudding-Britton model

Apart from destabilizing factors, the role of electrostatic stabilization in the Dudding-Britton model transition structures has also been shown by computational studies. Natural bond orbital (NBO) [53, 54, 55] data revealed that there is a stabilizing electrostatic interaction between the α- hydrogen of the aldehyde and O19 from the dioxanone moiety in the favored Dudding-Britton model transition states (Figure 7). The NBO program performs the analysis of a many-electron molecular wave function in terms of localized electron pair bonding units. That is, it transforms a given wave function into a localized form corresponding to the one-center ("lone pair") and two- center ("bond") elements of the common Lewis structure picture.[56] For instance and based on the NBO data, there is a stabilizing interaction between lone pair of O19 and the C-H anti bonding orbital (C31-H43 in (*R*)-2-chloropentanal or C31-H38 in (*R*)-2-chloro-2-phenylacetaldehyde) in the Dudding-Britton model.

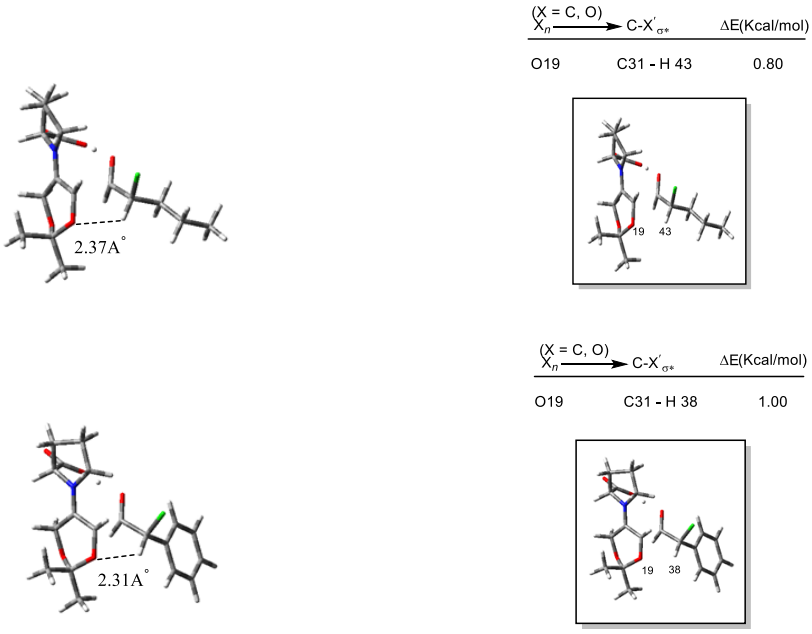


Figure 7. Stabilizing electrostatic interaction between α- hydrogen and O19 based on the Dudding-Britton model.

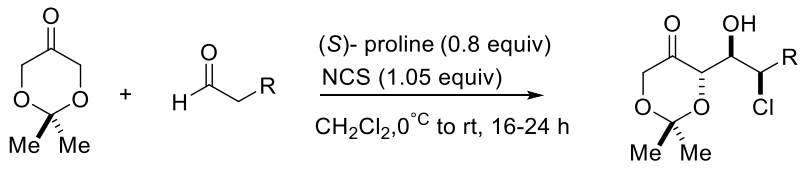
Even though the magnitude of these stabilizing interactions are not significant, they are bigger than similar interactions in the all polar Felkin-Anh model counterparts (Figure 8).

It should be noted that, such a stabilizing interaction does not exist in the Evans-Cornforth model.

Dudding-Britton model *Polar Felkin-Anh mode*

Figure 8. Comparing stabilizing electrostatic interaction between α- hydrogen and O19 in Dudding-Britton and Polar Felkin-Anh models.

Having considered all of the above factors, the Dudding-Britton is the best transition state model between dioxanone and different aldehydes in the proline-catalayzed chlorination/aldol reaction and leads to *syn*-chlorohydrins (Scheme 29). Moreover, the relative free energies (kcal/mol) of different transition state structures based on the polar Felkin-Anh, the Evans-Cornforth and the Dudding-Britton models are summarized in the Table 5, along with the diastereomeric ratio of the *syn*-chlorohydrin over the *anti*-chlorohydrin products based on the experimental results.



Scheme 29. Proline-catalayzed chlorination/aldol reaction

Remarkably, in the case of phenylacetaldehyde (Entry 3, Table 5), the relative free energy between the favored Dudding-Britton model and the disfavored Polar Felkin-Anh model is only 0.51 kcal/mol. Unlike other aldehydes, there is no destabilizing steric interaction between H2 of the enamine with β-hydrogen of 2-chloro-2-phenylacetaldehyde (there is no β-hydrogen in 2-chloro-2 phenylacetaldehyde). Besides, there is an ample distance between H2 of the enamine and the α-hydrogen of 2-chloro-2-phenylacetaldehyde in the Polar Felkin-Anh model (Figure 9). Consequently, the only factor that makes the Dudding-Britton transition state model slightly favorable over the Polar Felkin-Anh transition state model is the stabilizing hydrogen interaction between the α- hydrogen and O19 which was discussed in Part 3-6. This result shows the importance of an existing destabilizing steric interaction for distinguishing different transition state models.

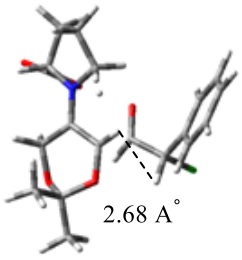
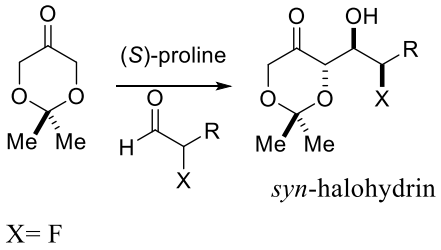


Figure 9. Ample distance between H2 of the enamine and α-hydrogen of 2-chloro-2-phenylacetaldehyde in the Polar Felkin-Anh model.

2-8-7 Replacing chlorine with fluorine in the proline-catalayzed chlorination/aldol reaction

In order to gauge the accuracy of diastereoselectivity, chlorine was replaced with fluorine and again *syn*-halohydrin formation was favored over *anti*- halohydrin formation based on the theoretical calculations (Scheme 30). Unlike the proline-catalyzed α-chlorination/aldol reaction, experimental results were not available in the proline-catalyzed α-fluorination/aldol reaction to validate the computational studies.



Scheme 30. Replacing fluorine instead of chlorine in the proline-catalayzed chlorination/aldol reaction.

Considering the fact that all mentioned destabilizing steric and electrostatic factors between α-halo aldehydes and the (*S*)-proline-derived enamine exist here again (which makes the Dudding-Britton model the most stable and favorable one), some new interactions were also considered by computational studies as follow. Replacing fluorine instead of chlorine increases destabilizing electrostatic interaction between the halogen and O atoms in the Evans-Cornforth transition state model. For one thing, the distance between the halogen and O atoms becomes greater from 3.14A° in the (*S*)-2-

chloropentanal to 2.74A° in the (S)-2-fluoropentanal and as a result the ρ (charge density) value increased from 0.009 to 0.02 au, confirmed by AIM calculations (Figure 10).

Table 6

The charge electron density(ρ), the Laplacian ($\nabla^2\rho$), kinetic energy density ($G_{(b)}$), potential energy density($V_{(b)}$) and the total electronic energy density (H_b) at the bond critical point (BCP) .

Bond	ρ	$\nabla^2\rho$	G_b	V_b	H_b
O—Cl	0.009	0.035	0.0080	-0.0071	0.0009

Table 7

The charge electron density(ρ), the Laplacian ($\nabla^2\rho$), kinetic energy density ($G_{(b)}$), potential energy density($V_{(b)}$) and the total electronic energy density (H_b) at the bond critical point (BCP) .

Bond	ρ	$\nabla^2\rho$	G_b	V_b	H_b
O—Cl	0.02	0.049	0.011	-0.0097	0.0013

Figure 10. . Increasing destabilizing electrostatic interactions between halogen and O atoms from (A): (*S*)-2-chloropentanal to (B): (*S*)-2-fluoreopentanal.

Apart from increasing the destabilizing interaction between oxygen from dioxanone and fluorine from α-fluoreo aldehyde, NBO data revealed that there is a stabilizing hydrogen interaction between the fluorine from the aldehyde and the hydrogen from diaxanone in the favored Dudding-Britton model (Figure 11).

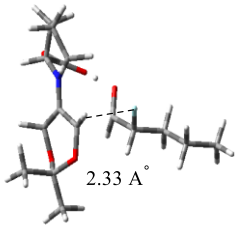


Figure 11. Stabilizing hydrogen bond interaction between fluorine and hydrogen from diaxanone moiety.

After replacing fluorine instead of chlorine and optimizing the Dudding-Britton transition states model of different aldehydes, the distance between halogen from the aldehyde and the hydrogen from dioxanone in favored transition states becomes shorter. As a result, a stabilizing hydrogen interaction can be revealed by NBO data (Figure 12).

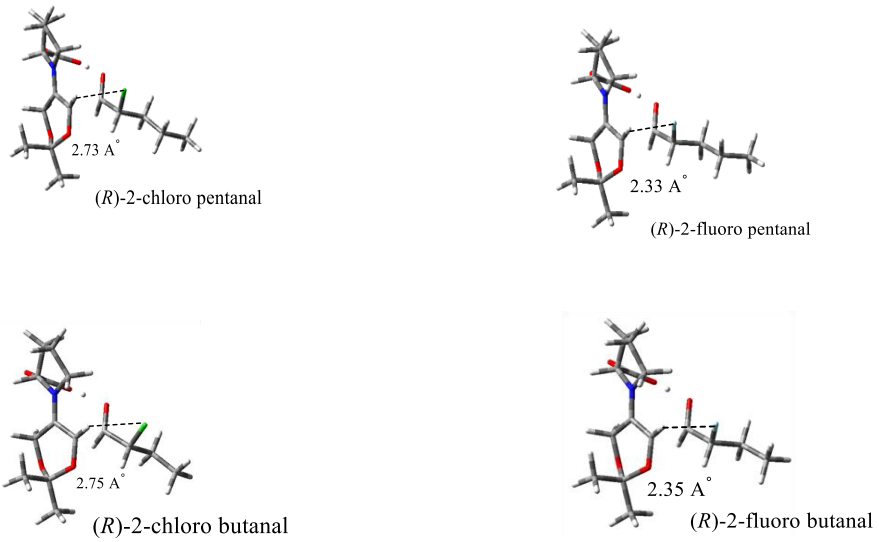


Figure 12. Increasing the distance between the halogen and hydrogen from dioxanone in α-fluoro aldehydes.

For instance, the stabilizing hydrogen interaction in (*R)*-2-chloro-2-phenylacetaldehyde is small and negligible while it becomes greater and considerable in (*R)*-2- fluoreo-2-phenylacetaldehyde (Figure 13).

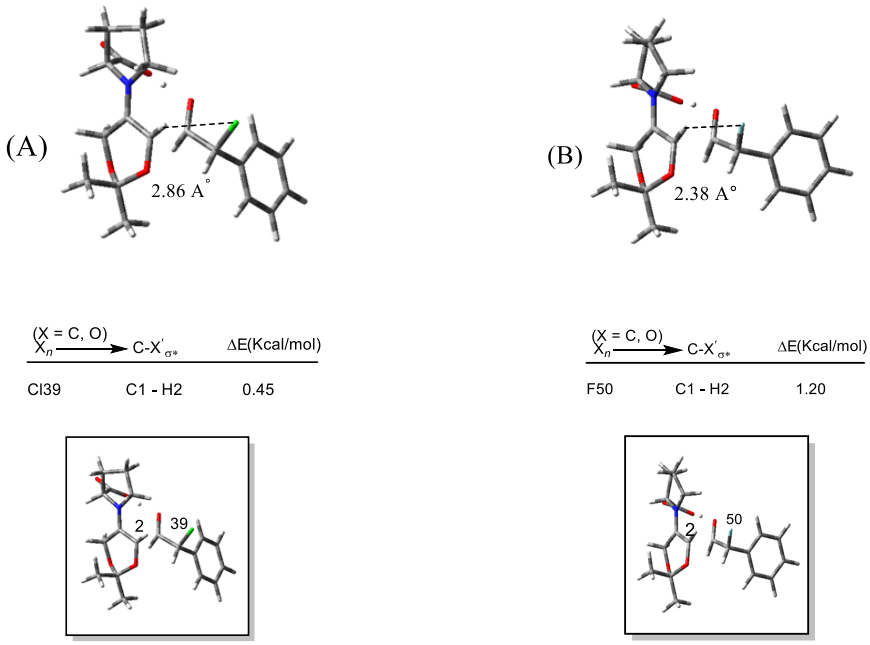


Figure 13. Stabilizing interaction between hydrogen of dioxanone and chlorine in A): *R*-2-chloro-2-phenylacetaldehyde, B): *R*-2- fluoro-2-phenylacetaldehyde.

The relative free energies (kcal/mol) of transition states between the enamine and 2-fluoropentanal based on: A) the Polar Felkin-Anh model B) the Evans-Cornforth model and C) the Dudding-Britton model are illustrated in Figure 14. Again, among different transition state models, the Dudding-Britton is the most stable one leads to *syn*-halohydrin product. The calculated relative free energies (kcal/mol) of different fluoro-aldehydes based on favored and disfavored transition state models have been summarized in the Table 8.

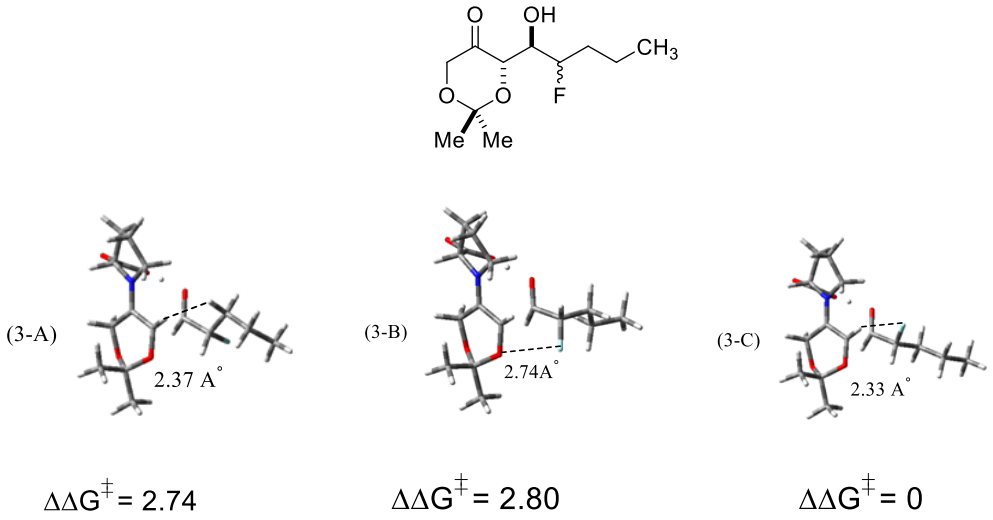


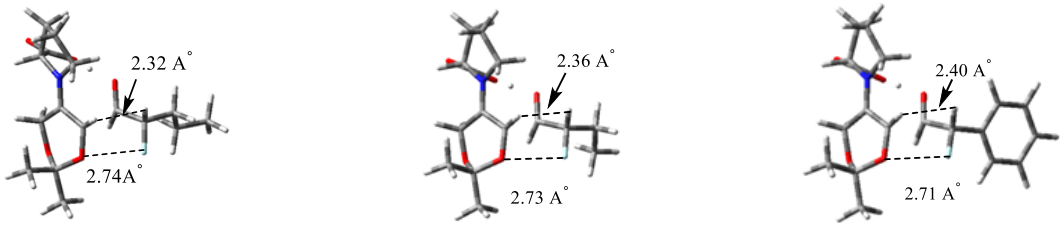
Figure 14. The relative free energies (kcal/mol) of transition state between the enamine and 2-fluoropentanal based on: A) polar Felkin-Anh model B) Evans-Cornforth model and C) Dudding-Britton model.

Table 8

	Relative Free energy			
Entry	Aldehyde	*Polar Felkin-Anh (kcal/mol)*	*Evans-Cornforth (kcal/mol)*	*Dudding-Britton (kcal/mol)*
1	Pentanal	2.74	2.80	0
2	Butanal	2.21	2.47	0
3	Phenylacetaldehyde	0.61	2.77	0
4	pent-4-enal	1.90	2.24	0

The difference in relative free energies between the Polar Felkin-Anh and the Evans-Cornforth models are smaller in Table 8 in comparison with the results in Table 5. This fact can be clarified by having closer look at both destabilizing steric and electrostatic interactions. As it was discussed in the Part 3-5, based on the Evans-Cornforth transition

state model of the reaction between different α-chloroaldehydes and (*S*)-proline-derived enamine, both steric and electrostatic destabilizing factors exist at the same time. Consequently, the Evans-Cornforth model was by far the least stable and had the most relative free energy among other proposed transition state models (Figure 6). Unlike α-chloroaldehydes, based on the Evans-Cornforth transition state model of the reaction between different α- fluoroaldehydes and (*S*)-proline-derived enamine, the steric interaction between the H2 of the enamine and the α-hydrogen of the aldehyde is ruled out and the only destabilizing factor is the electrostatic interaction between the O and fluorine atoms (Figure 15).

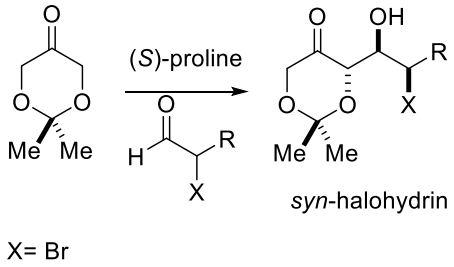


(S)-2-fluoropentanal (*S*)-2-fluorobutanal 2-fluoreo 2-phenylacetaldehyde

Figure 15. Destabilizing interaction between O and fluorine atoms based on Evans-Cornforth transition state model of the reaction between different α- fluoro aldehydes and (*S*)-proline-derived enamine.

Finally, we replaced bromine instead of chlorine to compare the relative free energies of different transition state structures of the reaction between the enamine fragment and α-bromoaldehydes. Here again, since there are no experimental results have been reported (after replacing bromine instead of chlorine), stereoselectivity of the final products

obtained by computational calculations and based on the most stable transition state model (according to the previous steric and electrostatic factors).



Scheme 31.Replacing bromine instead of chlorine in the proline-catalayzed chlorination/aldol reaction.

After optimizing different transition states between the enamine and different substrates of bromoaldehydes with wB97xd /6-31G (d) level of theory, the Evans-Cornforth model where halogen and oxygen atoms are facing each other was not observed in neither cases. Considering the fact that bromine is bulkier than chorine and fluorine, after optimizing transition states to the Evans-Cornforth model, they all turned and converted to the polar Felkin-Anh model. Hence, the only disfavored factor is the steric interaction between H2 of the enamine and β-hydrogen of aldehyde based on the polar Felkin-Anh model as mentioned earlier. The Dudding-Britton model was found again the best transition state to rationalize the *syn*-halohydrin formation. (Figure 16, Table 9).

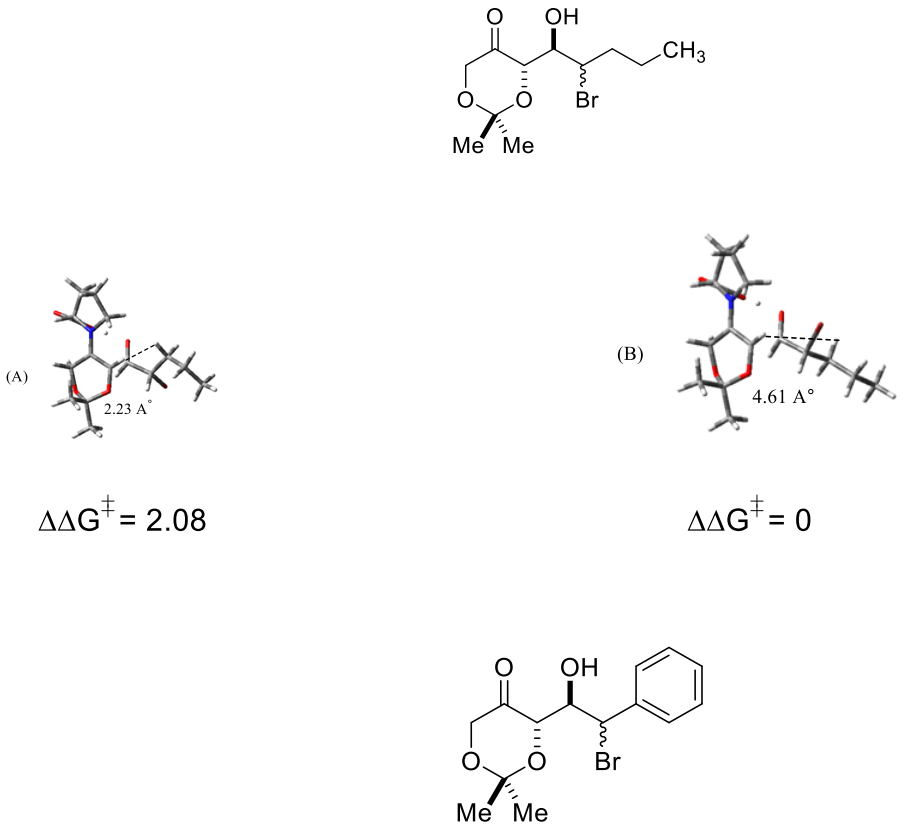


Figure 16. The relative free energies (kcal/mol) of transition state of bromopentanal and bromo phenylacetaldehyde based on A) The polar Felkin-Anh model and B)The Dudding-Britton model.

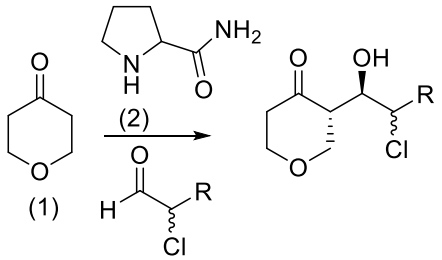
Table 9

	Relative Free energy		
Entry	Aldehyde	*Polar Felkin-Anh (kcal/mol)*	*Dudding-Britton (kcal/mol)*
1	Pentanal	2.080	0
2	Butanal	2.12	0
3	Phenylacetaldehyde	0.05	0
4	Pent-4-enal	1.54	0

2-8-8 Conclusions and future work

In summary, the theoretical investigations of "intractable pathologythe proline-catalyzed α-chlorination aldol reaction was pursued to determine the reasonable transition state in the reaction between the enamine and α-chloro aldehyde. Based on our DFT calculations (wB97XD/ 6-31G (d) level of theory), it was determined that the formation of the corresponding *syn*-chlorohydrin products is preferred. The existence of several studies of the relationship between the structural aspects of different α-haloaldehydes gave us the idea to explain the stereoselectivity of the final product through the chiral proline catalysts. The Dudding-Britton transition state model seemed to be useful for explanation of the stereoselectivity of the chlorohydrin product. All the studied cases driven from α-chloroaldehyde were in accordance with experimental results in terms of stereoselectivity of the chlorohydrin product. In other words, after computational modeling and based on experimental results, *syn*-chlorohyrine was found as a major product. Likewise, by replacing fluorine and bromine instead of chlorine and by comparing relative free energy of different transition state structures of the reaction between the enamin and α-haloaldehydes, the Dudding-Britton transition state model was again indicated to be the

best model for rationalizing the stereoselectivity of the final product. Both steric and electrostatic factors played important roles to make the Dudding-Britton model more preferred than the Polar Felkin-Anh and the Evans-Cornforth models. Computational modeling showed steric and electrostatic factors in disfavored models along with favored hydrogen bonding in the preferred transition state model. Replacing fluorine instead of chlorine increased disfavored electrostatic interaction between halogen and O atoms (disfavored electrostatic factor) as well as increased the distance between α hydrogen from aldehyde and H2 of enamine fragment (modifying steric factor) in the Evans-Cornforth model. After computational modeling of the Evans-Cornforth transition state, AIM theory was used to indicate the closed-shell (electrostatic) interactions between halogen and O atoms. Moreover, stabilizing hydrogen interaction between fluorine and hydrogen from diaxanone was revealed by NBO data in the favored Dudding-Britton model. In order to elucidate the stereoselectivity of the final product, (*S*)-proline and dioxanone could be replaced with *(S)*-pyrrolidine-2-carboxamide (2) and tetrahydro-pyran-4-one (1).



Computational modeling could be used and different transition state models could be tested. By calculating relative free energies of transition states and determining the lowest one, computational results could support the experimental observation in future research.

Moreover, considering the reaction mechanism precisely by computational studies could be the other interesting area for computational chemists.

In conclusion, we designed and proposed a new model to elucidate the stereoselectivity of the final product in the asymmetric organocatalytic aldehyde chlorination/aldol reaction. Moreover, this model is also useful to determine the stereoselectivity of the final product while the other halogens such as fluorine and bromine are replaced instead of chlorine.

3 Part two:

Theoretical energy barrier calculation of hydrogen splitting by chiral intramolecular phosphine boron frustrated Lewis pai

Abstract

Asymmetric hydrogenation of imines and enamines is one of the most important subjects in organic chemistry. After the discovery of frustrated Lewis pairs (FLPs) by Stephan[57], metal-free hydrogenation of imines and enamines has also been taken into account. Frustrated Lewis pairs (FLPs) consist of main-group element systems including sterically hindered Lewis acids and bases which are able to cleave molecular hydrogen heterolytically under mild reaction conditions.[58] FLPs have become beneficial catalysts for homogeneous hydrogenation without using transition-metal catalysis [59]. Intermolecular FLP systems involving chiral borones have been reported for enantioselective imine hydrogenation. On the other hand, intramolecular FLP systems which are able to undergo asymmetric hydrogenation of imines and enamines have been rarely reported. We designed a new intramolecular chiral binaphthyl-linked phosphine-boron FLP system, which is able to activate molecular hydrogen. In order to determine whether or not this new FLP system can split hydrogen, we calculated the energy barrier of the hydrogen activation step using (DFT) methods.

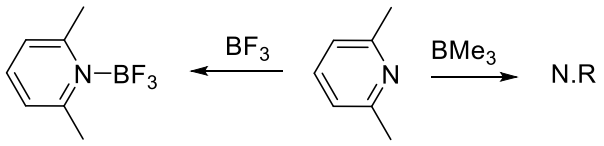
All transition states, substrates and products were optimized at both the B3LYP/6-31G(d) and the B3LYP-D3/6-31G(d) levels of theory.

Frustrated Lewis Pairs

3-1 Introduction

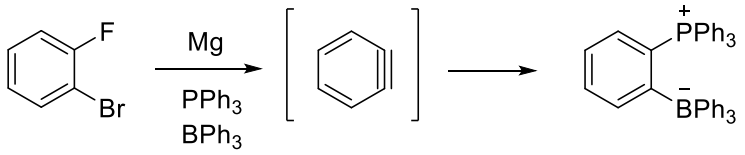
In 1923 G. N. Lewis suggested another way of looking at the reaction between H^+ and OH^- ions. He classified molecules that behave as electron-pair donors as bases and conversely electron-pair acceptor systems as acids. In the Lewis theory of acid-base reactions, the HOMO (highest occupied molecular orbital) of a Lewis base interacts with the LUMO (lowest unoccupied molecular orbital) of a Lewis acid to create a bonding molecular orbital. These concepts of Lewis acids and bases were used to rationalize numerous reactions. For instance, the aluminum ion is the metal and is a cation with an unfilled valence shell, and it is a Lewis acid. Water has lone-pair electrons and is an anion, thus it is a Lewis base. Lewis acid/base chemistry has been crucial to understanding of much of main-group and transition-metal chemistry and a guiding principle in understanding chemical reactivity in general. For example, by using Lewis acid/base chemistry, dissolving non-metal oxides such as CO_2 in water to form acids can be rationalized.

Even though much Chemistry can be considered in terms of the interaction of Lewis acids and bases, researchers have faced systems that appear to deviate from Lewis's principle. For example, in 1942 Brown and coworkers[60] realized that in the reaction between pyridines with simple borones, although most of these combinations of Lewis acids and bases formed classical Lewis adducts, lutidine formed a stable adduct with BF_3 but did not react with BMe_3 (Scheme 29).



Scheme 32. Treatment of lutidine with BMe_3 and BF_3 (N.R: no reaction).

Because of the steric conflict of the ortho-methyl groups of lutidine with the methyl groups of the borone, lutidine did not react with BMe_3. In 1959, Wittig and Benz[61] found that 1, 2-didehydrobenzene reacts with the mixture of the Lewis base triphenylphosphine and the Lewis acid triphenylborane to give the o-phenylene bridged phosphonium-borate (Scheme 33). They realized that the special nature of the bulky Lewis pairs had significant role that this reaction did not lead to the classical Lewis acid/base adduct.

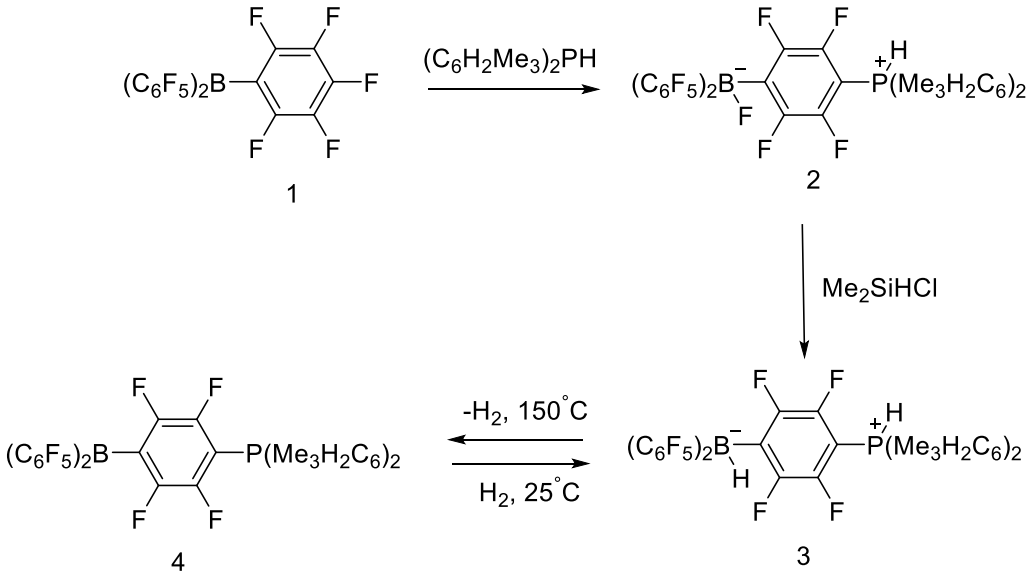


Scheme 33. Early FLP reagents.

3-2 Frustrated Lewis Pairs and H_2 Activation

The group of Stephan developed a concept for metal-free hydrogenation based on 'Frustrated Lewis pairs'. In this system, sterically hindered Lewis donors and very electrophilic Lewis acceptors are present, and their steric demands preclude formation of simple Lewis acid-base adducts. These non-self-quenching Lewis pairs allow the Lewis acidic and Lewis basic sites to react in a cooperative way towards other molecules such

as H_2 in a unique fashion[62]. As a starting point, they prepared a borane derivatives with electron donating phosphine or electron withdrawing phosphonium groups in the *para*-position to a Lewis acidic boron centre by the reaction of sterically hindered phosphine with the strong Lewis acid $B(C_6F_5)_3$.[63] The zwitterionic salt 2 was treated with Me_2SiHCl, generated 3 cleanly. The zwitterionic species 3 is an unusual example of a molecule containing both protic and hydridic fragments (Scheme 34). Species 3 was air and moisture stable and can release hydrogen by heating to 150°C, producing orange-red phosphino-borane 4. Because of the steric congestion at both the P and B centers, dimerization will not take place in solution and this molecule can be described as a sterically "frustrated Lewis pair". As a result, a frustrated Lewis pair can be used for metal-free activation of hydrogen in hydrogenation processes.

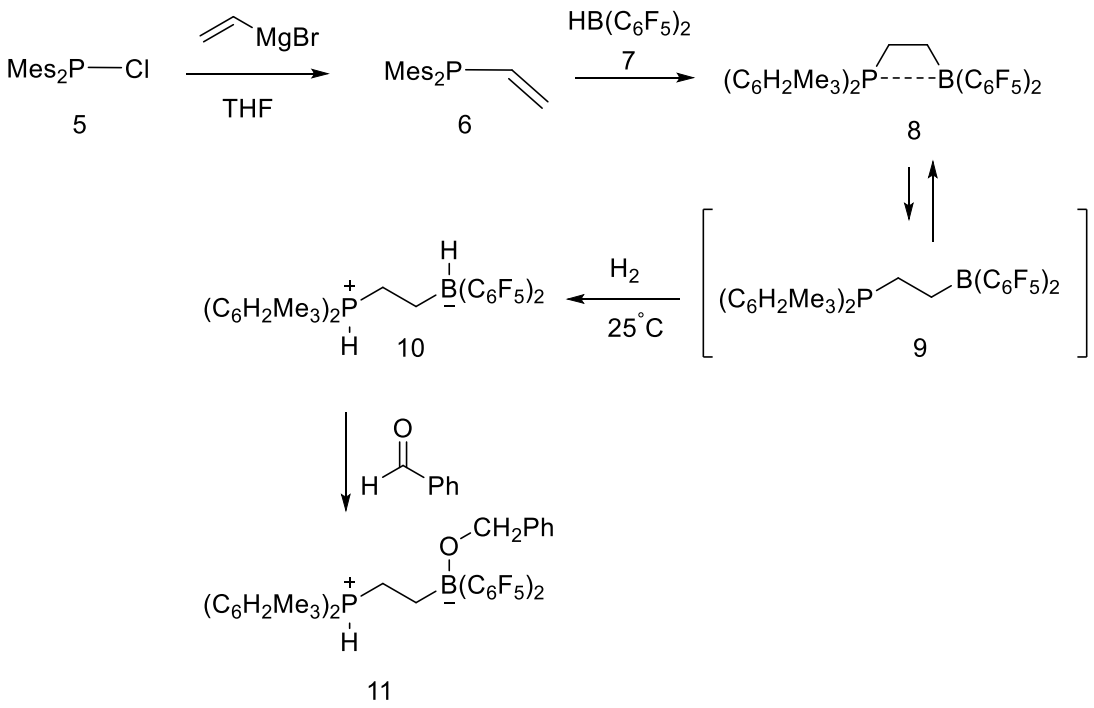


Scheme 34. Synthesis of phosphine-boranes and phosphonium-boranes by Stephan.

In general, frustrated Lewis pairs can be divided into “Intramolecular FLP" and " intermolecular FLP".

3-3 The Intramolecular FLP

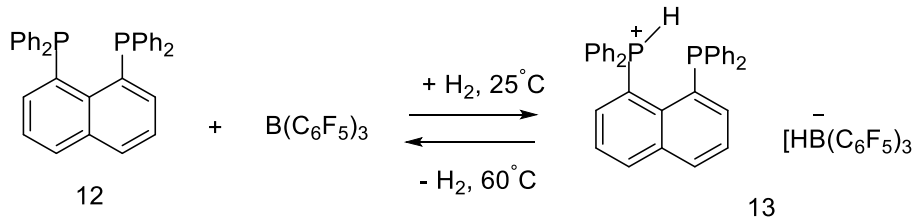
The Erker group synthesized a four-membered cyclic intramolecular phosphane–borane adduct which was able to activate dihydrogen and reduce benzaldehyde. [64] In order to synthesize this intramolecular FLP system, chlorodimesitylphosphane(5) was reacted with vinyl magnesium bromide to yield vinyldimesitylphosphane (6). Reaction of the (dimesityl)vinylphosphine with Piers' borane (7) produces the clean hydroboration product (8)/(9) (Scheme 35). Theoretical analysis revealed that there is a weak P···B interaction in this four-membered heterocyclic structure [(P···B) calcd. 2.21A$^{\circ}$]. This geometry is also supported by favorable π–π-stacking interactions between an electron-poor C_6F_5 arene ring on the boron and a parallel electron-rich mesityl substituent at phosphorus. Density functional theory (DFT) calculation also localizes an isomeric open chain of (9) which is only 7 Kcal/mol^{-1} above the cyclic (π -stacking stabilized) ground state of (8). It is assumed that the open isomers are responsible for the observed H_2-activation. While a solution of compound 8 in pentane was stirred in a dihydrogen atmosphere (1.5 bar) at room temperature, a large amount of white precipitate 10 was formed, confirmed by characteristic NMR spectral features. However, product 10 can rapidly reduce benzaldehyde to give the benzylalcohol 11.



Scheme 35. Synthesize and reactivity of intramolecular FLP by Erker.

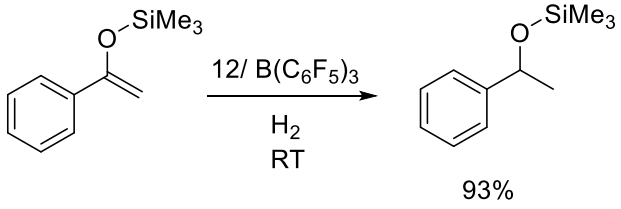
3-4 The Intermolecular FLP

The Erker group also synthesized an intermolecular frustrated Lewis pair based on 1,8 bis(diphenylphosphino) naphthalene (12) which is able of heterolytic H_2 cleavage.[65,66]Combination of this bidentate phosphine with $B(C_6F_5)_3$ in a 1:1 molar ratio, resulted in a non-quenched Lewis pair that activated H_2 to produce the phosphonium hydridoborate salt 13 (Scheme 36). There is a weak P-H---H-B interaction between the phosphonium cation and the hydridoborate anion in the salt (13) with a H--H distance of 2.08 A°.



Scheme 36. Reversible H_2 activation by $12/B(C_6F_5)_3$.

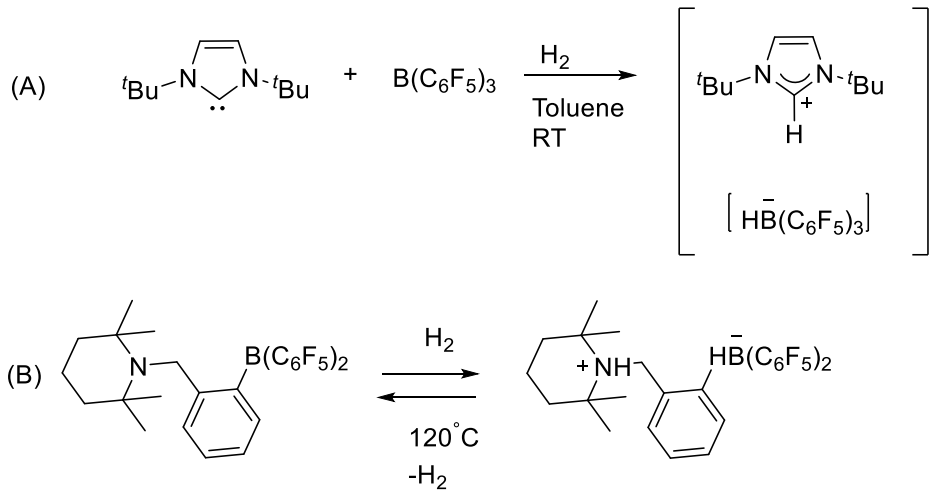
The above system is one of the rare examples of an observed reversible uptake/release of dihydrogen at a "frustrated Lewis pair"[67]. Heating a solution of the salt (13) in benzene at $60^{\circ C}$ resulted a formation of (12) and $B(C_6F_5)_3$, indicating stoichiometric loss of H_2. Since the $12+B(C_6F_5)_3/13$ FLP system can simply release hydrogen, it was used as a hydrogenation catalyst in a series of silyl enol ether as illustrated in Scheme 37.



Scheme 37. Hydrogenation catalyst of silyl enol ether.

3-5 Other FLP systems

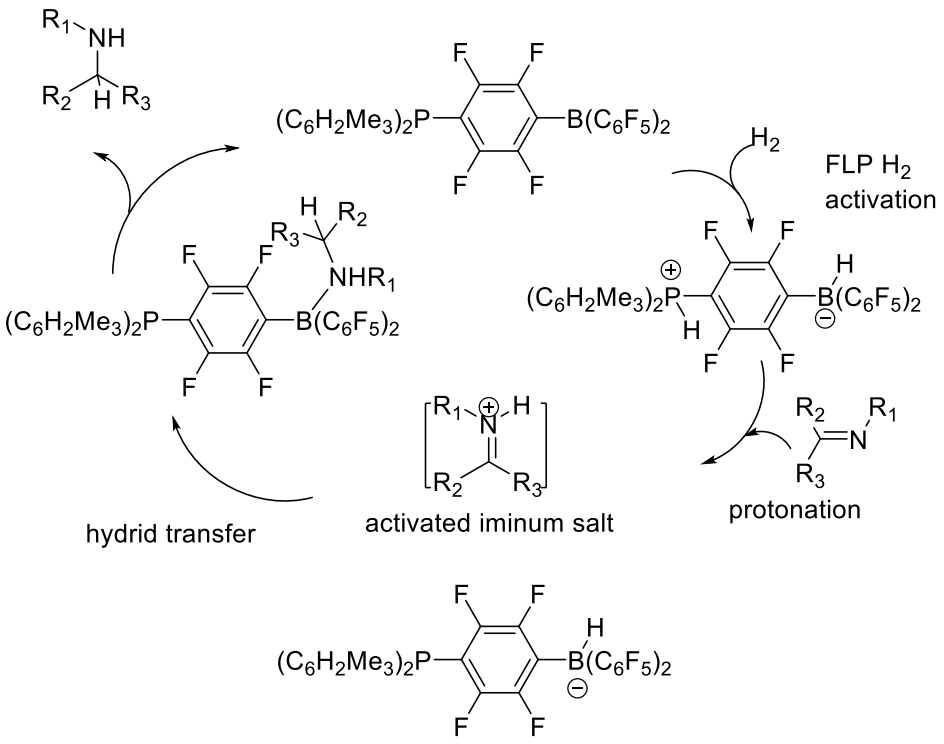
Other than intra and inter molecular FLP systems based on Phosphorous and Boron centers which were mentioned above, there are different frustrated Lewis pair systems which are able to activate dihydrogen based on Carbon/Boron and Nitrogen/Boron centers as shown in Scheme 38.



Scheme 38. FLP's systems based on A) Carbon/Boron and B) Nitrogen/Boron centers.

3-6 Mechanism of FLP hydrogenation

After the discovery of metal-free activation of hydrogen by the Frustrated Lewis pair, the application of this finding was used for hydrogenation catalysis reactions. It is noteworthy that for hydrogenation to be catalytic, proton and hydride transfer from a phosphonium hydridoborate to a substrate should be able to regenerate the frustrated Lewis pair. Studies to probe the mechanistic details for this metal-free hydrogenation have shown that the process is initiated by protonation of the imine followed by borohydride attack of the iminium salt intermediate[68] (Scheme 39).

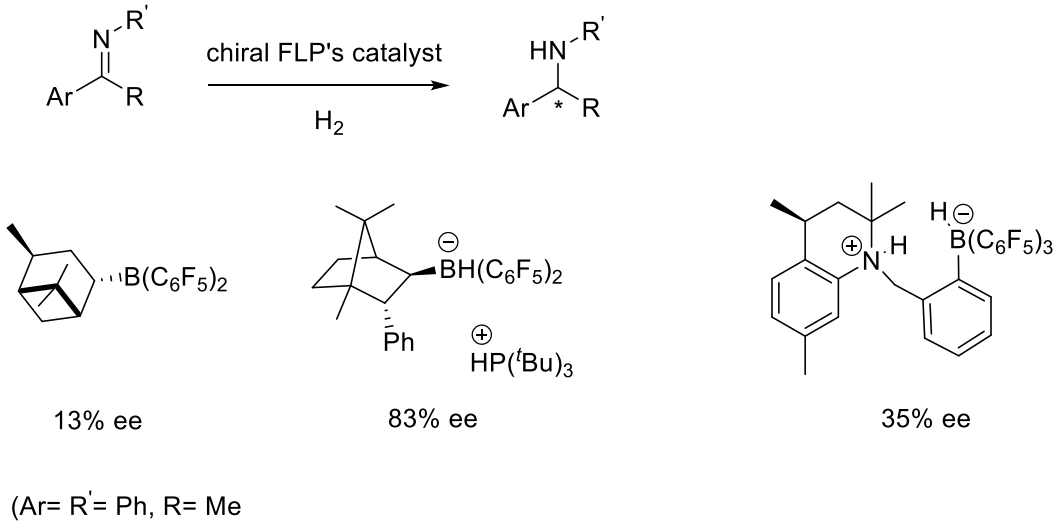


Scheme 39. Proposed mechanism for metal-free catalytic hydrogenations by using frustrated Lewis pair.

3-7 Asymmetric hydrogenation using frustrated Lewis pairs

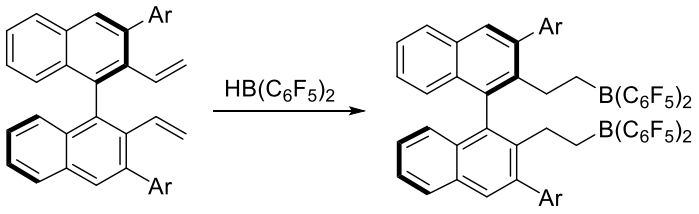
Preparing chiral amines by asymmetric hydrogenation of imines and enamines is one of the most important goals in organic chemistry[69]. The products include chiral α-carbons which are important in synthetic chemistry because of their applications as ligands, resolving agents, chiral auxiliaries, and building blocks. Since, using transition metal in catalyzed asymmetric hydrogenation of prochiral imines and enamines requires strict product purification (because of heavy-metal residuals in the products), replacing frustrated Lewis pairs would be more beneficial because of their ability as catalysts in homogeneous metal-free hydrogenations. In this regard, the number of frustrated Lewis

pairs which are able to asymmetric hydrogenation are few and limited to intermolecular FLP's with chiral Boron center[69] (Scheme 40).



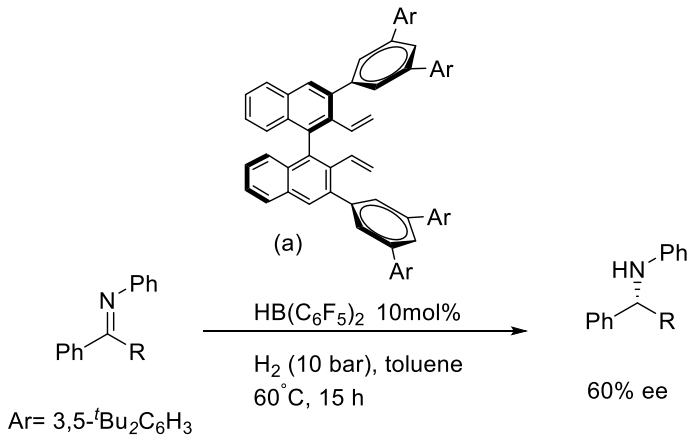
Scheme 40. Frustrated Lewis pairs with chiral Boron.

Recently the group of Du[70] has developed a new intermolecular borane-catalyzed metal-free asymmetric hydrogenation of imines, based on a binaphthyl backbone, with good asymmetric induction. In this reaction, the substrate could serve as the base-partner of the frustrated Lewis pair. The acid-partner of the frustrated Lewis pair can also be generated by direct hydroboration of chiral dienes bearing two terminal olefins with $HB(C_6F_5)_2$ (Scheme 41).



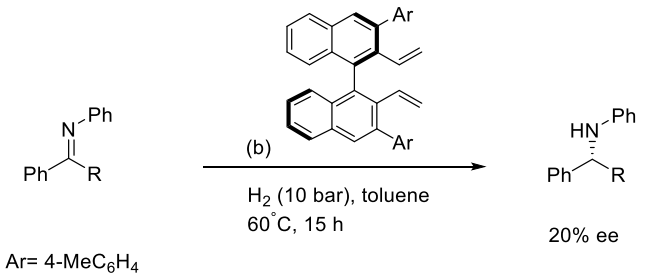
Scheme 41. Generating chiral borane catalyst for metal-free hydrogenation of imines.

The first step of converting an imine to an amine involves heterolytic H_2 splitting by the imine/borane FLP to generate an iminium hydridoborate ion. Then the protonated imine is activated to nucleophilic attack of the iminium carbon by the BH unit of the borohydride. The amine product is finally released by B–N bond dissociation under the heat condition. According to experimental studies, the steric bulkiness of the aryl substituent has direct impact on enantioselectivity. For instance, chiral dien frustrated Lewis pair catalyst (a) (while Ar= 3,5-^{t}Bu$_2$C$_6$H$_3$) was proved to be the optimal ligand in order to produce chiral amin product with 60%ee (Scheme 42).



Scheme 42. Chiral boran-catalyzed for asymmetric hydrogenation of imines.

On the other hand, by using less bulkier frustrated Lewis pair (b) with the same reaction condition, chiral amin was generated with only 20% ee (Scheme 43).

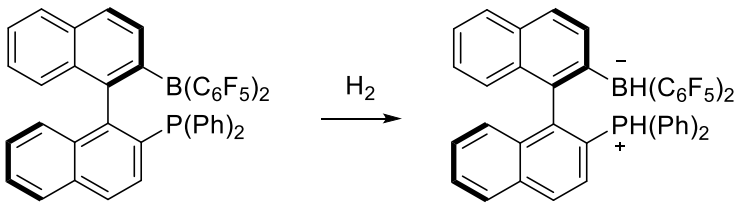


Scheme43. Hydrogenation of imine by less bulkier frustrated Lewis pair.

As solvent effect on hydrogenation of imine, mesitylene proved to be a suitable solvent to give 72% ee in $30^{\circ C}$ in the presence of (a) whereas by using hexane as a solvent and under the same reaction condition, imine is produced with only 55% ee.

3-8 Results and Discussion

We designed a new chiral binaphthyl-linked phosphine-boran as a novel intramolecular FLP system for enantioselective hydrogenation of imines and enamines. As an initial computational study, we measured the energy barrier of hydrogen activation by this new FLP system. The novelty of this (*S*) - intramolecular frustrated Lewis pair is the Lewis acid and base groups at the 2- and 2′-positions of the rigid asymmetric binaphthyl core (Scheme 44).



Scheme 44. (*S*)- Intramolecular Frustrated Lewis pair based on a chiral backbone.

In order to calculate the energy barrier of dihydrogen splitting by phosphino-borane FLP catalyst system, the transition states of the hydrogen activation was computed using density functional theory (DFT). The solvent effect was also taken into account by using different solvents such as toluene, diethyl ether and dichloromethane in integral equation formalism variant of the polarizable continuum model (IEFPCM) [71]. We applied three

different solvents to find out the solvent effect on the energy barrier of the hydrogen activation reaction and formation of phosphonium borohydride, which would be useful for experimental purposes. The B3LYP/6-31G(d) level of theory was chosen in order to optimize the transition state of hydrogen splitting by chiral phosphino-borane intramolecular frustrated Lewis pair. The B3LYP method has been demonstrated to give accurate results for energetic, structure and vibrational properties of molecules and solids.[72] Moreover, considering the fact that London-dispersion is crucial not only for structural stability of biomolecules or other large molecules but also for several thermochemical properties such as energy barrier, any accurate computational treatment requires a proper description of London-dispersion[73,74,75]. Based on that, additive dispersion correction such as D3 can correct behaviour of the dispersion energy per construction. Hence, B3LYP-D3 is not a new functional, but a mix of conventional functional and an add-on energy term, was also used to determine the accurate energy barrier.

3-8-1 Dihydrogen activation

We first investigated measuring of the energy barrier of dihydrogen activation via the intramolecular chiral phosphino-borane FLP catalyst with the B3LYP/6-31G (d) level of theory (Diagram 1). The active centers of phosphino-borane FLP catalyst are well prepared for simultaneous interaction with an H_2 molecule. This hydrogen activation leads to generation of the zwitterionic phosphonium -borohydride species (Figure 15, B). The transition state computed for the hydrogen activation process represents a fairly low activation barrier (20.02 kcal/mol) under the toluene solvent and in 300K. The formation

of phosphonium -borohydride (B) was found to be 2.48 kcal/mol exergonic (Diagram 1).

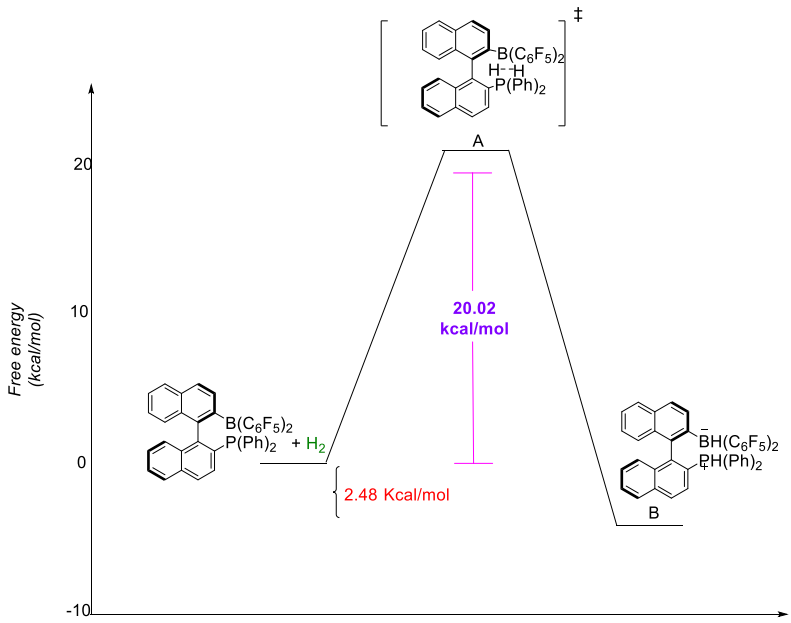
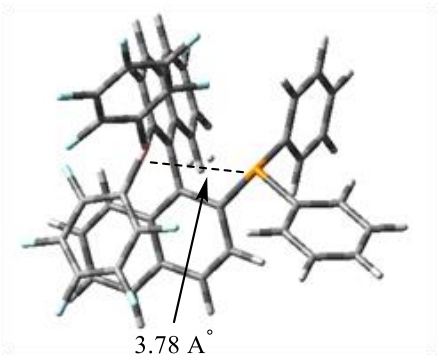


Diagram 1. Computational calculation of energy barrier of hydrogen splitting by FLP catalyst and toluene as a solvent with the B3LYP/6-31G (d) level of theory.

Based on optimized transition state structure (A), there is a stabilizing π-stacking interaction between binaphtyl and boron aromatic ring. As illustrated in Figure 17, the distance between the Lewis acid and Lewis base centers is 3.83 A°. The zwitterionic phosphonium -borohydride species (B) also revealed the relatively short BH···HP dihydrogen bond distance (2.29 A°).

Figure 17. Hydrogen splitting transition state by phosphino-borane FLP catalyst (A) and zwitterionic phosphonium -borohydride species (B).

Optimizing the transition state, regardless of solvent and in gas phase at 273K, indicated a slightly shorter distance between the Lewis acidic and basic centres (3.78 A°).



As discussed earlier, additive the dispersion correction such as D3, can correct behaviour of the dispersion energy per construction. Hence, we optimized the transition state for the hydrogen activation process by phosphino-borane FLP catalyst with B3LYP-D3/6-31G (d) level of theory in order to gauge the accuracy of the calculated energy barrier . Computational studies showed that the energy barrier of hydrogen splitting via phosphino -borane FLP catalyst with B3LYP-D3/6-31G(d) level of theory is relatively similar to

previous work with B3LYP/6-31G(d) and reasonable for experimental purposes (Diagram 2).

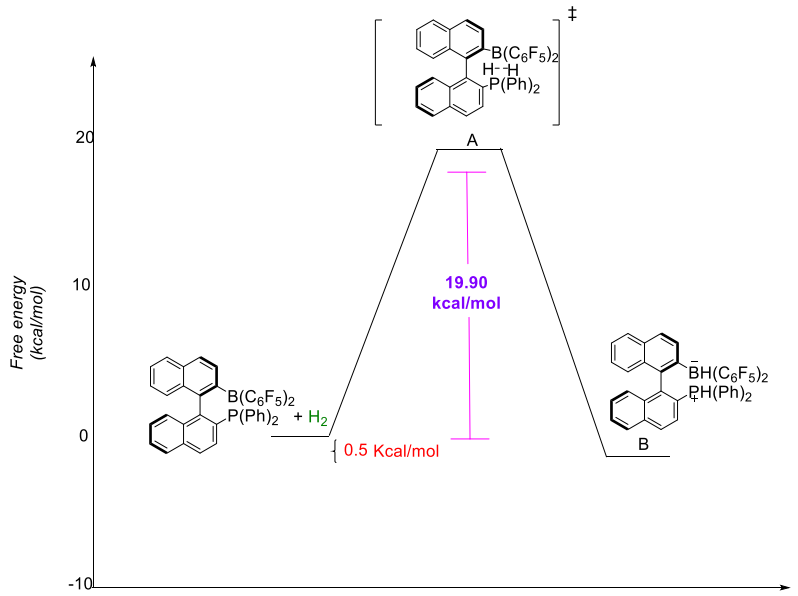
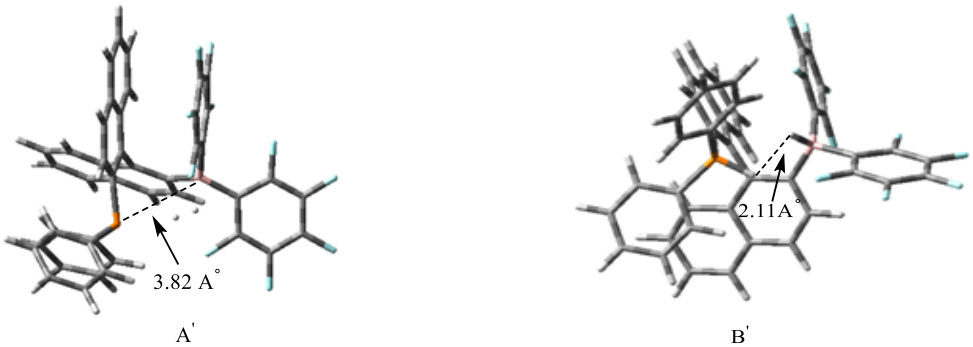


Diagram 2. Computational calculation of energy barrier of hydrogen splitting by FLP catalyst and toluene as a solvent with B3LYP-D3/6-31G (d) level of theory.

As shown in Figure 18, the distance between Lewis acid and Lewis base centers in transition state remained unchanged (3.82 A°), whereas the BH⁻⁻HP dihydrogen bond distance in phosphonium -borohydride species became shorter from 2.29 to 2.11 A°.



A' B'

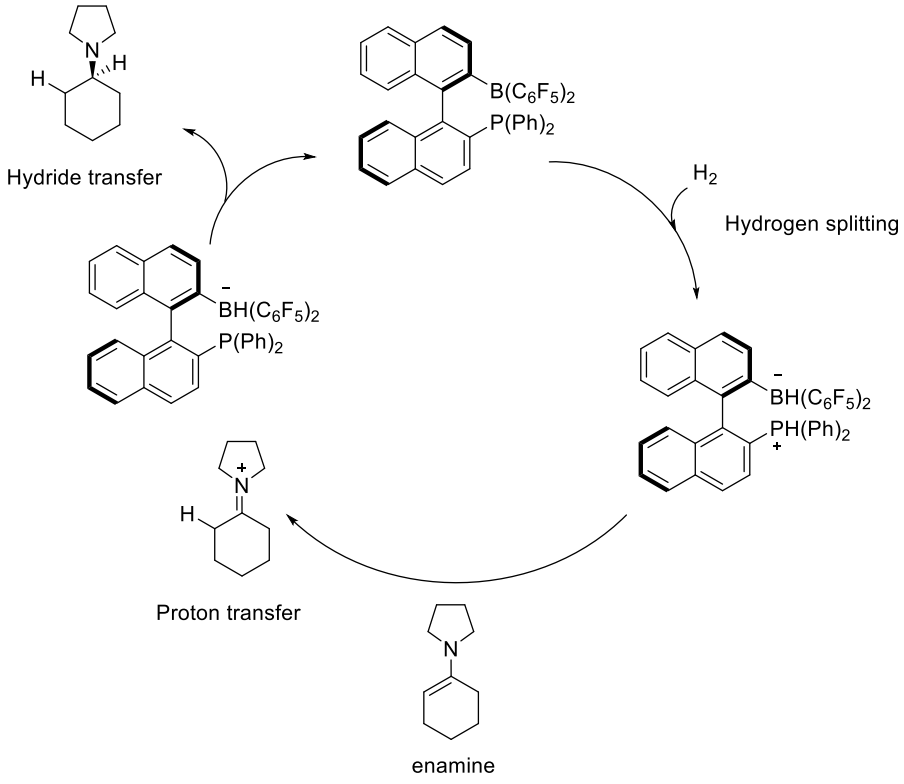
Figure 18. Hydrogen splitting transition state by phosphino-borane FLP catalyst (A') and zwitterionic phosphonium -borohydride species (B') under B3LYP-D3/6-31G(d) level of theory.

In order to consider the solvent effect, toluene was replaced with dichloromethane and diethyl ether and hydrogen splitting energy barrier was calculated again for each case. After computational studies and calculations, the energy barrier of hydrogen activation via the intramolecular chiral phosphino-borane FLP catalyst entails a reasonably low activation barrier for all cases (~ 20 kcal/mol).

3-9 Conclusion and future work

In this thesis, the novel intramolecular Frustrated Lewis pair based on chiral backbone for the asymmetric hydrogenation of imines and enamines was designed. The ability of hydrogen splitting by this new FLP system was examined by computational modeling and calculating the hydrogen activation energy barrier . The transition state of hydrogen splitting as well as zwitterionic phosphonium -borohydride were optimized with both B3LYP/6-31G(d) and B3LYP-D3/6-31G(d) level of theory. Over the past seven years, FLP catalyzed metal-free hydrogenation of imines has been successfully realized in organic chemistry. Based on that, fairly low computed energy barrier indicates that hydrogen splitting would be feasible by new intramolecular frustrated Lewis pairs. This new FLP system could be a catalyst for asymmetric hydrogenation of imines and enamines. In order to consider the solvent effect on hydrogen splitting energy barrier by the chiral FLP system, three different solvents (toluene, dichloromethane , diethyl ether) were also taken into account and after optimizing transition states, products and starting materials, it was found that the barrier for the hydrogen activation process is fairly low (~ 20 kcal/mol) for all cases.

The mechanism for the asymmetric hydrogenation of enamine also could be considered by computational studies along with experimental observations. Based on FLP-type hydrogenation of enamines[76], there are two steps for the hydrogen transfer process. First is the protonation of enamine to generate an ion pair intermediate and second, the hydride transfer which leads to amine product and regenerates the catalyst.



By using density functional theory (DFT) and characterizing transition states of protonation and hydride transfer steps, the free energy diagram for generating amine product can be finalized. Relative Gibbs free energies can be calculated for the most stable ion pair intermediate and amine product based on different solvents including

toluene, dichloromethane and diethyl ether. As stated earlier, hydrogen transfer from hydrogenated FLP (B in diagram 3) to the enamine substrate takes place in two steps. By characterizing transition states of protonation (C) and hydride transfer (E) steps, the barrier (E1 and E_2) can be computed to determine the rate-determining step in the catalytic cycle.

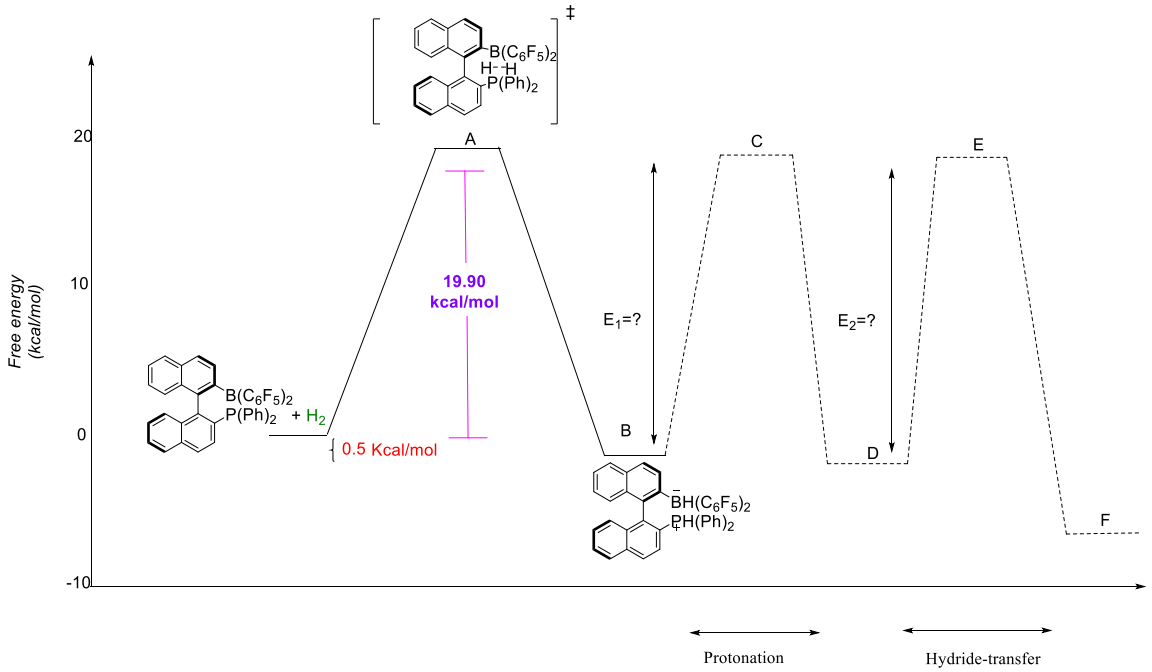


Diagram 3. Proposed computed free energy diagram for converting enamine to amine by FLP asymmetric hydrogenation.

In summary, a novel (*S*) - intramolecular phosphine boron frustrated Lewis pair molecule was designed for asymmetric hydrogenation of different imines and enamines. After computationally calculating the energy barrier of the hydrogen activation step, it was revealed that, newly designed FLP molecule is able to split hydrogen and generate zwitterionic phosphonium-borohydride.

4 Experimental

General. All the calculations were performed using the Gaussian 09[77].

For "A DFT study of organocatalytic aldol reaction" (Part two), all transition states, substrates and products were optimized at wB97xd /6-31G (d) level of theory. The reason to use this level of theory is to consider better the dispersion interactions as well hydrogen bonding and van der Waals interactions than conventional DFT. The most stable transition state model was chosen by comparing the sum of electronic and thermal free energies of all transition state models (see appendix). All calculations involve the salvation model IEFPCM with dichloromethane (ε=8.93) as a solvent and temperature was set to 273K. The NBO 4.0 program was used as implemented in the Gaussian 09 package. AIM200 was used to determine the nature of interactions in bond critical points.

For" Theoretical energy barrier calculation of hydrogen splitting by chiral intramolecular phosphine boron frustrated Lewis pair" (Part three), all transition states, substrates and products were optimized at B3LYP /6-31G(d)[51] and B3LYP-D3/6-31G(d)[52,53,54] level of theory. The reason to use B3LYP-D3/6-31G(d) level of theory is consider London-dispersion which is crucial not only for structural stability of biomolecules or other large molecules but also for several thermochemical properties such as energy barrier. All calculations involve the solvation model *IEFPCM* with different types of solvent; toluene(ε=2.38) , dichloromethane (ε=8.93) and diethyl ether (ε=4.33) and temperature was set to 300K. Moreover, the respective product complexes immediately following from the transition states were located using the intrinsic reaction coordinate (IRC) method [78,79] and confirmed to be minima by appearance of only real vibrational modes.

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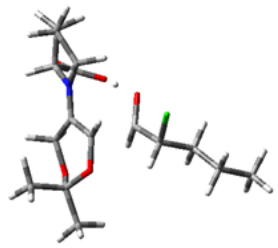
.

6 **Appendix**: Thermochemical and coordinate data for all computed structures

TS- (*R*)-2-chloro pentanal (Dudding-*Britton model*)



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.419457 (Hartree/Particle)

Thermal correction to Energy= 0.439429

Thermal correction to Enthalpy= 0.440293

Thermal correction to Gibbs free energy= 0.372892

Sum of electronic and zero-point Energies= -1515.690962

Sum of electronic and thermal Energies= -1515.670990

Sum of electronic and thermal Enthalpies= -1515.670125

Sum of electronic and thermal Free Energies= -1515.737526

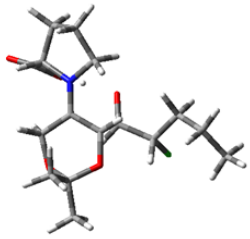
0 1

C 0.04816300 0.84407500 -0.91219200

H	0.27911400	0.34215800	-1.84615600
C	-1.20040600	0.68666000	-0.31719400
N	-1.96635600	-0.37065600	-0.58604700
C	-3.13838400	-0.75623000	0.20735500
H	-3.87444100	0.05359000	0.21229000
C	-1.85095900	-1.16166600	-1.82578500
H	-1.07758600	-1.92368900	-1.70514800
H	-1.57569100	-0.50361700	-2.65428700
C	-3.24268400	-1.76623100	-1.98172300
H	-3.22470100	-2.69007000	-2.56389500
H	-3.90902600	-1.05301000	-2.47810100
C	-3.68594100	-1.99060600	-0.53695500
H	-4.76615600	-2.07761600	-0.41200300
H	-3.21696700	-2.89682600	-0.13746700
C	-1.57879900	1.62924700	0.79374500
H	-2.50567000	2.15767100	0.52591100
H	-1.76234700	1.09379000	1.72900700
O	0.76366300	2.01667000	-0.77555700
O	-0.52496800	2.52081500	1.08093100
C	0.11606200	3.06401600	-0.05395200
C	1.21684000	3.96188900	0.47075200
H	0.78486400	4.81214000	1.00527100
H	1.82134600	4.33564500	-0.35972600
C	-0.85287200	3.80040200	-0.97625200
H	-1.56078200	3.12068400	-1.45956100
H	-0.28856900	4.31081600	-1.76135000
H	-1.41690100	4.54444600	-0.40589200
C	0.92606500	-0.50288700	0.35687100
H	0.88802800	0.19426500	1.21420700

C	2.33151900	-0.47857000	-0.24380800
O	0.28690700	-1.59465800	0.40187200
C	-2.86576900	-1.12121900	1.67077700
O	-1.66597700	-1.53490800	2.01448600
O	-3.78412600	-1.07458200	2.46489600
H	-0.94685400	-1.54311400	1.27672100
H	1.85695800	3.39506300	1.15241800
C	3.32278900	-1.06916100	0.75818900
H	3.15750900	-0.54317300	1.70886200
C	4.79046400	-0.92071300	0.35906700
H	4.96820600	-1.43802100	-0.59090200
H	5.00869700	0.14117700	0.18576700
H	2.61027200	0.54607600	-0.49563500
Cl	2.38230400	-1.40800000	-1.80766300
H	3.07236500	-2.12280000	0.93056400
C	5.73267400	-1.47483500	1.42524100
H	5.55232000	-2.54326900	1.59300900
H	6.78002500	-1.35437000	1.12777300
H	5.59475300	-0.95906800	2.38307700

TS- (*S*)-2-chloro pentanal (*Polar Felkin-Anh model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.420364 (Hartree/Particle)

Thermal correction to Energy= 0.439988

Thermal correction to Enthalpy= 0.440853

Thermal correction to Gibbs Free Energy= 0.374377

Sum of electronic and zero-point Energies= -1515.687740

Sum of electronic and thermal Energies= -1515.668117

Sum of electronic and thermal Enthalpies= -1515.667252

Sum of electronic and thermal Free Energies= -1515.733728

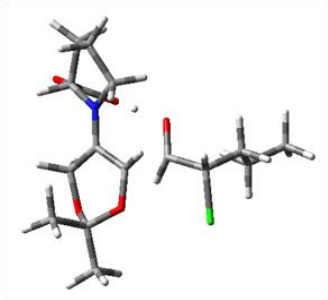
0 1

C	-0.33820100	0.67781400	0.76519900
H	-0.70148400	0.06779400	1.58674000
C	1.02159900	0.67093200	0.44511500
N	1.79677000	-0.36300700	0.75748500
C	3.14062500	-0.57647400	0.20593500
H	3.78155600	0.27794700	0.44356200
C	1.48572000	-1.31785700	1.83869800
H	0.84055500	-2.10939100	1.45124200
H	0.96774900	-0.79852000	2.64905000
C	2.86043500	-1.83682100	2.24699800
H	2.80275300	-2.82402000	2.71028200
H	3.32661200	-1.14467400	2.95607100
C	3.63111600	-1.84819800	0.92815300
H	4.71510100	-1.83636700	1.04967600
H	3.35762400	-2.73308900	0.34244500
C	1.54280200	1.76086700	-0.45278800

H	2.36990800	2.28457100	0.04887400
H	1.93152300	1.35005600	-1.38858700
O	-1.09345000	1.82504800	0.61660600
O	0.51194400	2.64255800	-0.83468300
C	-0.38095300	2.99031300	0.20235500
C	-1.40613400	3.92013800	-0.41117600
H	-0.92665800	4.85262400	-0.72084300
H	-2.18598400	4.14851300	0.31983100
C	0.32979600	3.61398200	1.40162300
H	0.96786200	2.89615200	1.92563000
H	-0.41588000	3.98139700	2.11165800
H	0.94794600	4.45421100	1.07176800
C	-0.80828800	-0.53361700	-0.79536200
H	-0.67031800	0.26057300	-1.54868200
C	-2.27876900	-0.70416600	-0.40716500
H	-2.69279500	0.25561600	-0.09587400
O	-0.07322600	-1.56913700	-0.82921000
C	3.22159000	-0.78823700	-1.31064100
O	2.15994600	-1.21050700	-1.95909600
O	4.28999600	-0.61235000	-1.86187300
H	1.29473500	-1.34268600	-1.40936900
H	-1.86089400	3.44244800	-1.28332700
C	-2.52820800	-1.80223200	0.62564700
H	-1.60271900	-1.93067400	1.19803800
C	-3.67242500	-1.49917900	1.59691900
H	-3.44079500	-0.56988300	2.13509900
H	-3.69641600	-2.29527800	2.35101300
Cl	-3.16144000	-1.06119200	-1.98298500
H	-2.69538500	-2.75685100	0.11654400

C	-5.05088000	-1.37858700	0.95008700
H	-5.31260200	-2.29293200	0.40441900
H	-5.82121700	-1.20843600	1.71061000
H	-5.09433100	-0.54474300	0.24094700

TS- (*S*)-2-chloro pentanal (*Evans-Cornforth model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.419545 (Hartree/Particle)

Thermal correction to Energy= 0.439370

Thermal correction to Enthalpy= 0.440235

Thermal correction to Gibbs Free Energy= 0.372701

Sum of electronic and zero-point Energies= -1515.684073

Sum of electronic and thermal Energies= -1515.664248

Sum of electronic and thermal Enthalpies= -1515.663383

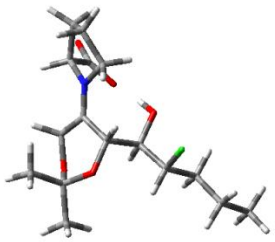
Sum of electronic and thermal Free Energies= -1515.730917

0 1

C	-0.01365000	1.06820900	0.88397700
H	-0.19094600	0.78795800	1.91822700
C	1.17479100	0.68070400	0.25738600
N	1.87400400	-0.36924900	0.67889100
C	2.96347100	-0.98866900	-0.08671000
H	3.74445500	-0.24934800	-0.28903900
C	1.79508100	-0.90216400	2.05341000
H	0.97363900	-1.61824200	2.11933600
H	1.61295000	-0.08290200	2.75362500
C	3.15667800	-1.56085100	2.24941200
H	3.12390300	-2.35016400	3.00351900
H	3.89462800	-0.81336300	2.55838200
C	3.48761600	-2.09075900	0.85584000
H	4.55045000	-2.27368700	0.69225000
H	2.94294800	-3.02321700	0.67072200
C	1.53463000	1.34291700	-1.04515200
H	2.55009600	1.76076500	-0.97797000
H	1.52461900	0.62000000	-1.86578000
O	-0.58133600	2.29356000	0.59552600
O	0.58542000	2.31985800	-1.40089400
C	0.13338000	3.11311000	-0.32261900
C	-0.87253100	4.08578900	-0.90229200
H	-1.35418500	4.64579700	-0.09659400
H	-1.63524300	3.53685500	-1.46090800
C	1.27910500	3.82507800	0.39702000
H	1.92064400	3.13217200	0.94988300
H	0.86570600	4.54051000	1.11321400
H	1.89386500	4.36874600	-0.32672600
C	-1.11166100	-0.44163700	0.01511900

H	-1.20313000	0.08839900	-0.94714300
C	-2.39438200	-0.42392300	0.87118900
O	-0.46712400	-1.53636500	0.08312400
C	2.57722000	-1.60841700	-1.43488600
O	1.32757200	-1.95775200	-1.64544300
O	3.45256300	-1.81095400	-2.25238200
H	0.65915200	-1.74693600	-0.88952300
H	-0.37140800	4.78885800	-1.57338100
C	-3.19495300	-1.71757400	0.69518800
H	-2.56450600	-2.51800500	1.09808100
C	-3.59583300	-2.06287800	-0.73880200
H	-4.17007700	-1.23658300	-1.17445900
H	-2.69128100	-2.17953700	-1.34689000
H	-2.14885000	-0.30345500	1.92713600
Cl	-3.44552900	1.00564600	0.45927300
H	-4.08585400	-1.65579800	1.33169700
C	-4.42161400	-3.34610000	-0.80284300
H	-3.87026100	-4.19385100	-0.37857600
H	-5.35817900	-3.24219000	-0.24201100
H	-4.67800900	-3.59779800	-1.83781200

Product-2-chloro pentanal



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=calcfc freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.422381 (Hartree/Particle)

Thermal correction to Energy= 0.442535

Thermal correction to Enthalpy= 0.443400

Thermal correction to Gibbs Free Energy= 0.374925

Sum of electronic and zero-point Energies= -1515.716112

Sum of electronic and thermal Energies= -1515.695958

Sum of electronic and thermal Enthalpies= -1515.695093

Sum of electronic and thermal Free Energies= -1515.763568

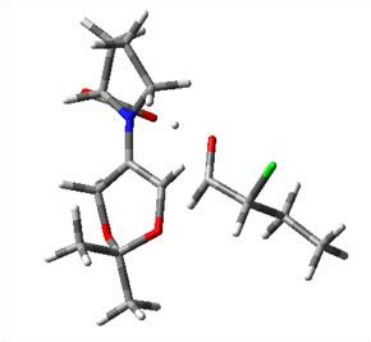
0 1

C	0.15049000	0.67799100	-0.71494700
H	0.17043800	0.31359900	-1.74322300
C	-1.22571200	0.60222300	-0.13209800
N	-2.08898300	-0.26072500	-0.53835300
C	-3.27656100	-0.64164100	0.25156600
H	-3.82140900	0.26611700	0.52356700
C	-2.00027700	-1.08980900	-1.76140300
H	-1.45807400	-2.00462500	-1.50904700
H	-1.46513000	-0.55355200	-2.54370000
C	-3.46762400	-1.34649800	-2.07442200
H	-3.58997300	-2.21399200	-2.72591700
H	-3.89477600	-0.47148100	-2.57470600
C	-4.09488900	-1.54599000	-0.69152200

H	-5.15489600	-1.28907200	-0.66752100
H	-3.99538000	-2.58816200	-0.37575600
C	-1.48855100	1.47808400	1.05811300
H	-2.42587000	2.03334400	0.91256600
H	-1.59556000	0.85228400	1.94809600
O	0.71994300	1.96509400	-0.71217200
O	-0.39445400	2.33073100	1.29330100
C	0.12734200	2.95232800	0.13698100
C	1.25636900	3.84475100	0.60911800
H	0.86011600	4.66434900	1.21475800
H	1.78381400	4.26332600	-0.25173000
C	-0.93402300	3.71990800	-0.64908600
H	-1.67737800	3.05801800	-1.10471000
H	-0.44693100	4.27302500	-1.45631000
H	-1.44960200	4.42901900	0.00531100
C	1.00786700	-0.29970700	0.17158700
H	1.02962500	0.13548700	1.18248700
C	2.46551200	-0.31965400	-0.28237400
O	0.48003300	-1.58722000	0.16869100
C	-2.87426400	-1.38994600	1.57615600
O	-1.64726400	-1.54188600	1.82325300
O	-3.85059600	-1.74978800	2.24193000
H	-0.29602200	-1.61280000	0.78477500
H	1.95730100	3.25943600	1.21055100
C	3.34059300	-1.14211300	0.65382900
H	3.16067900	-0.74665500	1.66331100
C	4.83796300	-1.07466100	0.35792000
H	5.04125300	-1.51410100	-0.62535300
H	5.15010400	-0.02324200	0.30540600

H	2.82604300	0.70833900	-0.34804900
Cl	2.58572200	-0.96082400	-1.99420000
H	2.99221900	-2.18048400	0.65423500
C	5.65823700	-1.80224700	1.42089300
H	5.37305800	-2.85920200	1.48406900
H	6.72898500	-1.75772300	1.19384400
H	5.50685000	-1.35572800	2.41103000

TS- (*R*)- 2-chlorobutanal (*Dudding-Britton model*)



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.390477 (Hartree/Particle)

Thermal correction to Energy= 0.409321

Thermal correction to Enthalpy= 0.410186

Thermal correction to Gibbs Free Energy= 0.345448

Sum of electronic and zero-point Energies= -1476.415843

Sum of electronic and thermal Energies= -1476.397000

Sum of electronic and thermal Enthalpies= -1476.396135

Sum of electronic and thermal Free Energies= -1476.460873

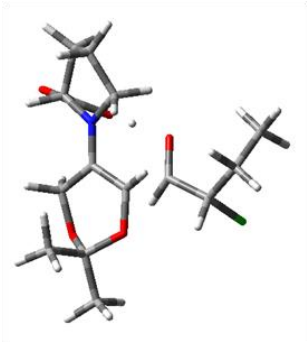
0 1

C	0.52283600	0.62517200	-0.86698300
H	0.73479900	0.00553000	-1.73213800
C	-0.77916500	0.75342500	-0.39258400
N	-1.70836200	-0.16480200	-0.66067600
C	-2.99741100	-0.25225600	0.03423700
H	-3.54944000	0.68620100	-0.07595600
C	-1.64316500	-1.06932100	-1.82370500
H	-1.06142800	-1.95771300	-1.56684500
H	-1.15852700	-0.55661300	-2.65879200
C	-3.10910400	-1.39197600	-2.09219000
H	-3.23062300	-2.34522100	-2.61130400
H	-3.56168900	-0.60194100	-2.70043600
C	-3.72281600	-1.40330400	-0.69311800
H	-4.80357800	-1.25472900	-0.68242500

H	-3.49905700	-2.35258400	-0.19385200
C	-1.06303500	1.84293000	0.60592200
H	-1.83590300	2.51633100	0.20697700
H	-1.43698400	1.43427400	1.54856700
O	1.43634000	1.65256100	-0.74292700
O	0.11702100	2.53539000	0.94497200
C	0.94833600	2.85678400	-0.15055700
C	2.15449000	3.56561100	0.42868100
H	1.85364800	4.52218100	0.86443700
H	2.89270500	3.75037200	-0.35608600
C	0.22744900	3.69015900	-1.20772300
H	-0.54395000	3.11735800	-1.73112300
H	0.95150200	4.03550400	-1.95041200
H	-0.24032100	4.56173000	-0.74007200
C	1.01042000	-0.74274800	0.58188000
H	1.01700800	0.01970200	1.38259000
C	2.44915800	-1.01807000	0.14589200
O	0.17760400	-1.69471200	0.62463900
C	-2.93198900	-0.55886500	1.53490400
O	-1.86657400	-1.15543100	2.02280800
O	-3.89523900	-0.29267800	2.22586900
H	-1.09998600	-1.35074900	1.36385900
H	2.60650000	2.94303900	1.20576500
C	3.20423400	-1.69203100	1.29210700
H	3.03938200	-1.06971500	2.18137600
C	4.70328000	-1.83616300	1.05161000
H	5.18798400	-2.26940600	1.93266400
H	4.91424600	-2.48881300	0.19840500
H	5.16521100	-0.86107700	0.85785200

H	2.93874600	-0.08407100	-0.13488400
Cl	2.49063000	-2.06812800	-1.33950700
H	2.74324700	-2.66493000	1.49504500

TS- (*S*)- 2-chlorobutanal (*Polar Felkin-Anh model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.390953 (Hartree/Particle)

Thermal correction to Energy= 0.409643

Thermal correction to Enthalpy= 0.410507

Thermal correction to Gibbs Free Energy= 0.346246

Sum of electronic and zero-point Energies= -1476.413368

Sum of electronic and thermal Energies= -1476.394678

Sum of electronic and thermal Enthalpies= -1476.393813

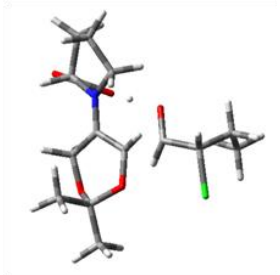
Sum of electronic and thermal Free Energies= -1476.458074

0 1

C	0.58369800	0.67202700	-0.94039000
H	0.72986700	0.09159300	-1.84570000
C	-0.70462000	0.83089500	-0.42280400
N	-1.65867600	-0.06003700	-0.67219300
C	-2.92972700	-0.13168900	0.06053900
H	-3.47463600	0.81115200	-0.04566000
C	-1.64016700	-0.96623400	-1.83733400
H	-1.05531800	-1.85672600	-1.59610000
H	-1.18223600	-0.45748200	-2.68952600
C	-3.11632000	-1.28093300	-2.05475800
H	-3.25917500	-2.23548200	-2.56573700
H	-3.58457200	-0.49101900	-2.65106400
C	-3.68270800	-1.28312000	-0.63626900
H	-4.76176500	-1.12986800	-0.58970200
H	-3.44561900	-2.23041100	-0.13941900
C	-0.92498500	1.90919900	0.60348600
H	-1.70281500	2.60068300	0.24761000
H	-1.26399400	1.49011400	1.55435900
O	1.51907300	1.68365600	-0.83788800
O	0.27933700	2.57601100	0.90308600
C	1.07626500	2.89190700	-0.21869600
C	2.31700300	3.57111800	0.32140700
H	2.05188700	4.52797900	0.77913400
H	3.02803300	3.75149400	-0.48901400
C	0.33382900	3.74910100	-1.24122400
H	-0.47339000	3.20044300	-1.73577100
H	1.03558000	4.08073700	-2.01102600
H	-0.09199900	4.62927600	-0.75038300
C	1.08879500	-0.71457600	0.45316000

H	1.18848400	0.03987900	1.25232800
C	2.45178700	-1.06622200	-0.15298800
H	2.91854100	-0.15724200	-0.53134200
O	0.20437300	-1.62207800	0.55799200
C	-2.82813800	-0.42492600	1.56240800
O	-1.75707400	-1.02511700	2.02986000
O	-3.77443500	-0.14363000	2.27078200
H	-1.00639700	-1.24076600	1.35198100
H	2.78642300	2.93057700	1.07309000
C	2.46370200	-2.15419100	-1.22317900
H	1.73540000	-1.84567400	-1.98392600
C	2.15311000	-3.58044900	-0.77497800
H	2.15608900	-4.24851500	-1.64320400
H	2.90741000	-3.94780800	-0.07184100
H	1.17626100	-3.63646000	-0.29165100
Cl	3.53735200	-1.52993100	1.25931100
H	3.44435600	-2.12955800	-1.71128600

TS- (*S*)- 2-chlorobutanal (*Evans-Cornforth model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.390865 (Hartree/Particle)

Thermal correction to Energy= 0.409480

Thermal correction to Enthalpy= 0.410344

Thermal correction to Gibbs Free Energy= 0.345959

Sum of electronic and zero-point Energies= -1476.408802

Sum of electronic and thermal Energies= -1476.390188

Sum of electronic and thermal Enthalpies= -1476.389323

Sum of electronic and thermal Free Energies= -1476.453709

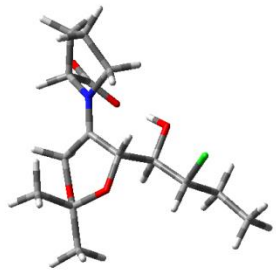
0 1

C	-0.58501200	0.67702300	0.88385300
H	-0.67569900	0.26075200	1.88285200
C	0.68098600	0.83812000	0.31222900
N	1.71902400	0.10562900	0.70465500
C	2.99223000	0.02887500	-0.02296000
H	3.43306000	1.02693700	-0.10943400
C	1.80118500	-0.54225900	2.02829700
H	1.31747100	-1.52020600	1.98461800
H	1.28909600	0.07706400	2.76906800
C	3.30288000	-0.64602400	2.27180900
H	3.55049000	-1.45437900	2.96314300
H	3.68250800	0.29440100	2.68501100
C	3.86481300	-0.87584200	0.87017000
H	4.92164000	-0.62578200	0.76843200
H	3.72667500	-1.92328700	0.57976800
C	0.79727900	1.70194400	-0.91460400

H	1.56441000	2.47357200	-0.75124300
H	1.10250300	1.10949100	-1.78189600
O	-1.57855700	1.60365900	0.63781500
O	-0.44560900	2.26107900	-1.26804000
C	-1.21481300	2.71489700	-0.17286300
C	-2.50253100	3.25906300	-0.75618500
H	-3.19627400	3.51911800	0.04753100
H	-2.96421600	2.50214600	-1.39584700
C	-0.47212800	3.75345900	0.66793600
H	0.37910100	3.32295700	1.20368400
H	-1.15736500	4.17379700	1.40903200
H	-0.10735900	4.56086300	0.02588200
C	-0.97350700	-1.05675200	-0.15528200
H	-1.26236800	-0.51348000	-1.06987400
C	-2.15676300	-1.64120400	0.64058600
O	0.05382900	-1.80776000	-0.15433400
C	2.93309900	-0.55222700	-1.44081600
O	1.92251800	-1.32086700	-1.78044500
O	3.85728800	-0.32705900	-2.19646300
H	1.19436900	-1.46264000	-1.06410000
H	-2.29679600	4.15424400	-1.34981800
C	-2.39010000	-3.11216700	0.28155600
H	-1.48698500	-3.64327200	0.59884300
C	-2.65786300	-3.39107400	-1.19444100
H	-3.54734200	-2.86144600	-1.55114800
H	-1.80669000	-3.09160300	-1.81504200
H	-1.96686600	-1.56532500	1.71221300
H	-3.21781800	-3.48342500	0.89550200
Cl	-3.68705300	-0.69500700	0.35742900

H -2.82310500 -4.46218200 -1.35001400

Product- 2-chlorobutanal



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=calcfc freq=noraman

wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.394344 (Hartree/Particle)

Thermal correction to Energy= 0.413162

Thermal correction to Enthalpy= 0.414026

Thermal correction to Gibbs Free Energy= 0.349227

Sum of electronic and zero-point Energies= -1476.440442

Sum of electronic and thermal Energies= -1476.421624

Sum of electronic and thermal Enthalpies= -1476.420759

Sum of electronic and thermal Free Energies= -1476.485558

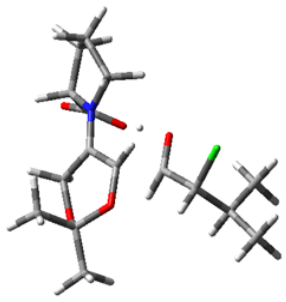
0 1

C -0.55425900 0.43721500 0.65304900

H	-0.59757800	-0.04256700	1.63180400
C	0.85769300	0.64926100	0.20518700
N	1.81945200	-0.10341600	0.60948100
C	3.11369000	-0.19845300	-0.09382400
H	3.51468400	0.80952500	-0.22818100
C	1.77340200	-1.07097600	1.72881900
H	1.41588400	-2.02487700	1.33294000
H	1.09224400	-0.71984200	2.50279200
C	3.23247600	-1.12512200	2.15942000
H	3.44653700	-2.03473700	2.72440100
H	3.46223900	-0.26031000	2.79023000
C	3.99801000	-1.05487600	0.83448100
H	4.99215200	-0.61988200	0.94641900
H	4.11544300	-2.05402000	0.40633400
C	1.06329800	1.68276200	-0.86331000
H	1.88310000	2.35692500	-0.57823700
H	1.33787800	1.18411000	-1.79675000
O	-1.32946000	1.61036600	0.72301400
O	-0.13362700	2.37902700	-1.11265700
C	-0.83750400	2.77156900	0.04817800
C	-2.05324300	3.53767800	-0.43069900
H	-1.74485400	4.47118500	-0.90928200
H	-2.70334100	3.77181100	0.41620800
C	0.02311200	3.58705300	1.01152300
H	0.82419000	2.99224700	1.46184700
H	-0.60766700	3.95889100	1.82309500
H	0.46984700	4.44004300	0.49208800
C	-1.16062500	-0.55477600	-0.40767300
H	-1.17001500	-0.01725400	-1.36844000

C	-2.62743300	-0.84960800	-0.10491400
O	-0.42979000	-1.73663000	-0.47922600
C	2.95142100	-0.85523900	-1.51515500
O	1.79113900	-1.16793600	-1.89623400
O	4.02607200	-0.98690900	-2.10988300
H	0.38874800	-1.56932200	-1.01253700
H	-2.60913100	2.93066100	-1.15053800
C	-3.28345100	-1.68091000	-1.20014200
H	-3.07853000	-1.15701900	-2.14297200
C	-4.79031700	-1.85113500	-1.03824600
H	-5.20708500	-2.37843700	-1.90251800
H	-5.03753200	-2.42940400	-0.14213400
H	-5.29074700	-0.87849200	-0.96331800
H	-3.15246500	0.09767400	0.02811800
Cl	-2.78404900	-1.69296900	1.51258200
H	-2.78361600	-2.65254300	-1.26190600

TS- (*R*)- iso-propyl chloroaldehyde (*Dudding-Britton model*)



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=278

****

Thermochemistry

****

Zero-point correction= 0.418810 (Hartree/Particle)

Thermal correction to Energy= 0.439360

Thermal correction to Enthalpy= 0.440240

Thermal correction to Gibbs Free Energy= 0.371618

Sum of electronic and zero-point Energies= -1515.691777

Sum of electronic and thermal Energies= -1515.671227

Sum of electronic and thermal Enthalpies= -1515.670347

Sum of electronic and thermal Free Energies= -1515.738969

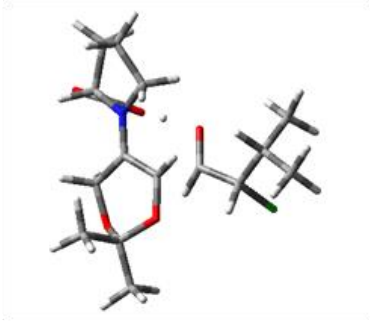
0 1

C	-0.24195000	0.86165300	0.87314500
H	-0.47257100	0.36457300	1.81022800
C	1.03878900	0.77636800	0.32908600
N	1.86411700	-0.21563800	0.65799600
C	3.08160400	-0.54832100	-0.08997800
H	3.75121600	0.31646300	-0.12332900
C	1.76772200	-0.96914000	1.92330800
H	1.06396700	-1.79600100	1.80694700
H	1.40990700	-0.30562700	2.71492000
C	3.19767000	-1.44972600	2.14825000

H	3.23402600	-2.34743900	2.76912300
H	3.78508600	-0.66440700	2.63529600
C	3.70846700	-1.69530300	0.72955500
H	4.79586000	-1.69042700	0.64207100
H	3.33538800	-2.65679000	0.35956000
C	1.38958400	1.70832600	-0.79983700
H	2.28040200	2.29476500	-0.53026500
H	1.62195400	1.15569400	-1.71442700
O	-1.01638600	1.99107600	0.69550400
O	0.29467200	2.53086700	-1.13464500
C	-0.40730000	3.05923400	-0.02922900
C	-1.54071300	3.88431100	-0.60161100
H	-1.14107200	4.74759200	-1.14023000
H	-2.18862300	4.23853200	0.20438400
C	0.49287500	3.86521000	0.90475300
H	1.22490200	3.23468700	1.41810400
H	-0.12179300	4.35345300	1.66566400
H	1.02818900	4.63216800	0.33710600
C	-0.97757800	-0.56030700	-0.38503800
H	-0.91905500	0.09003400	-1.27783600
C	-2.42134000	-0.56623200	0.11881700
O	-0.27553500	-1.61578900	-0.33260500
C	2.87481500	-1.01036900	-1.53749400
O	1.71355800	-1.51520500	-1.89014400
O	3.81376300	-0.95087800	-2.30639600
H	0.97326600	-1.53397600	-1.17089200
H	-2.12978200	3.27116100	-1.28920600
C	-3.38332300	-1.11836900	-0.95062300
H	-3.15235600	-0.51839800	-1.84283200

C	-4.84281000	-0.84823800	-0.58043100
H	-5.50165700	-1.13556200	-1.40717700
H	-5.14189300	-1.42591300	0.30146300
H	-5.01067500	0.21357300	-0.36671000
C	-3.15775500	-2.58934600	-1.29926300
H	-2.11402800	-2.78714300	-1.55795300
H	-3.42732200	-3.23837100	-0.45848000
H	-3.78637800	-2.86892100	-2.15183300
H	-2.71812300	0.45659000	0.35580800
Cl	-2.55533900	-1.48293700	1.68413800

TS- (*S*)- iso-propyl chloroaldehyde (*Polar Felkin-Anh model*)



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=278

****

Thermochemistry

****

Zero-point correction= 0.419064 (Hartree/Particle)

Thermal correction to Energy= 0.439605

Thermal correction to Enthalpy= 0.440485

Thermal correction to Gibbs Free Energy= 0.371932

Sum of electronic and zero-point Energies= -1515.690351

Sum of electronic and thermal Energies= -1515.669810

Sum of electronic and thermal Enthalpies= -1515.668930

Sum of electronic and thermal Free Energies= -1515.737483

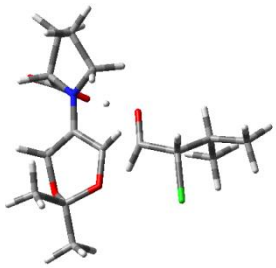
0 1

C	-0.33925900	0.79195600	0.85134100
H	-0.67320800	0.21377000	1.70715500
C	0.99546800	0.71646000	0.44389300
N	1.73647300	-0.35159200	0.71911300

C	3.03011900	-0.64319700	0.08752800
H	3.73736600	0.16581800	0.29344600
C	1.43908500	-1.28280700	1.82567900
H	0.71476100	-2.02746400	1.48863100
H	1.01686700	-0.72815700	2.66752100
C	2.79972300	-1.89601500	2.13831200
H	2.70600200	-2.87982300	2.60289600
H	3.36066200	-1.24236200	2.81428600
C	3.47632100	-1.95206800	0.77038500
H	4.56400200	-2.02051200	0.81709400
H	3.09855300	-2.80917100	0.20206100
C	1.50661900	1.76775200	-0.50390800
H	2.38962700	2.25667600	-0.06737800
H	1.80909200	1.32476700	-1.45664800
O	-1.04753900	1.97239900	0.73485500
O	0.49573200	2.69306100	-0.83220400
C	-0.31426300	3.09731100	0.25115600
C	-1.33711800	4.05732800	-0.31881700
H	-0.84152500	4.96388300	-0.67638900
H	-2.06231200	4.33062500	0.45190600
C	0.49601300	3.71236900	1.39035300
H	1.13499200	2.97720200	1.88863300
H	-0.18736900	4.12480700	2.13738600
H	1.12701700	4.51881800	1.00520800
C	-0.97632600	-0.40815600	-0.65558100
H	-0.86405800	0.38533100	-1.41422000
C	-2.42942900	-0.51525300	-0.17595100
H	-2.74195800	0.45000500	0.22267800
O	-0.27272400	-1.46323100	-0.74749500

C	3.01322200	-0.84688300	-1.43243700
O	1.89563300	-1.20987300	-2.02040300
O	4.05642400	-0.72540600	-2.04306500
H	1.05942800	-1.29620600	-1.42036100
H	-1.86179800	3.58175300	-1.15214500
C	-2.73420400	-1.62994000	0.83129100
H	-1.93666800	-1.54417200	1.58256500
C	-2.67968000	-3.04951300	0.26244600
H	-2.76686500	-3.77626200	1.07818000
H	-3.50814900	-3.22809500	-0.43188100
H	-1.73963700	-3.22411300	-0.26385500
C	-4.06750000	-1.37419000	1.53792000
H	-4.08719600	-0.38812000	2.01591800
H	-4.90311100	-1.42604200	0.82993400
H	-4.23967400	-2.12958100	2.31270500
Cl	-3.45606600	-0.67757500	-1.69554500

TS- (*S*)- iso-propyl chloroaldehyde *(Evans-Cornforth model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=278

****

Thermochemistry

****

Zero-point correction= 0.418241 (Hartree/Particle)

Thermal correction to Energy= 0.438934

Thermal correction to Enthalpy= 0.439815

Thermal correction to Gibbs Free Energy= 0.370407

Sum of electronic and zero-point Energies= -1515.685994

Sum of electronic and thermal Energies= -1515.665300

Sum of electronic and thermal Enthalpies= -1515.664420

Sum of electronic and thermal Free Energies= -1515.733828

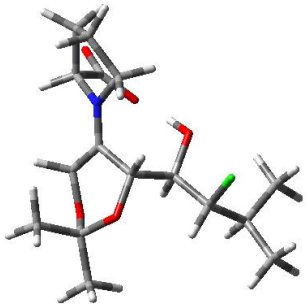
0 1

C	-0.22981700	0.87479100	0.86480200
H	-0.47690800	0.44329200	1.83052900
C	1.06403800	0.72128400	0.35335700
N	1.84116900	-0.28916500	0.72931800
C	3.07884600	-0.67664500	0.03956300
H	3.78965500	0.15529800	0.05208700
C	1.67078700	-1.01163500	2.00600000
H	0.92308600	-1.79758700	1.88207100
H	1.33275500	-0.31352000	2.77629700
C	3.06304400	-1.57125200	2.27973600
H	3.02799500	-2.46376400	2.90812300
H	3.67965600	-0.81703800	2.77954400

C	3.60346200	-1.85722800	0.88056000
H	4.69123100	-1.92305600	0.82968400
H	3.18072500	-2.79368800	0.49960300
C	1.48088200	1.59941800	-0.79567000
H	2.41405100	2.12196900	-0.53675300
H	1.67010200	1.00773100	-1.69563700
O	-0.92054700	2.05173900	0.65268600
O	0.45510100	2.49501900	-1.15304100
C	-0.22649700	3.07055200	-0.05711700
C	-1.28621500	3.97784400	-0.64746500
H	-1.92915600	4.36651700	0.14652900
H	-1.89780300	3.41292400	-1.35607300
C	0.71670800	3.81495000	0.88786200
H	1.38024800	3.13680000	1.43260900
H	0.12773100	4.36915300	1.62364000
H	1.32975800	4.52230900	0.32133600
C	-1.01874700	-0.61828600	-0.29952600
H	-1.10565700	0.03345000	-1.18424600
C	-2.35802300	-0.89909300	0.41295100
O	-0.23195900	-1.61958100	-0.31915600
C	2.93541000	-1.11681300	-1.42236400
O	1.77366100	-1.55871000	-1.84932000
O	3.92219400	-1.10010600	-2.13075400
H	0.99951900	-1.54307400	-1.16697300
H	-0.81623700	4.81757000	-1.16677100
C	-2.95056400	-2.24823600	-0.03549700
H	-2.15296200	-2.96068200	0.20378100
C	-3.21988500	-2.32812000	-1.53851800
H	-3.57456800	-3.33079200	-1.80125900

H	-3.98948800	-1.61107800	-1.84531500
H	-2.31335600	-2.13173100	-2.12042400
C	-4.18725500	-2.62830000	0.77883600
H	-3.99696900	-2.55065400	1.85573500
H	-5.04180900	-1.98668200	0.53739200
H	-4.47459500	-3.66286500	0.56078200
H	-2.21061700	-0.92862300	1.49435100
Cl	-3.54465900	0.45209900	0.12857400

Product- iso-propyl chloroaldehyde



%nprocshared=8

%mem=2500MB

opt=calcfc freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=278

****

Thermochemistry

****

Zero-point correction= 0.422116 (Hartree/Particle)

Thermal correction to Energy= 0.442823

Thermal correction to Enthalpy= 0.443703

Thermal correction to Gibbs Free Energy= 0.374089

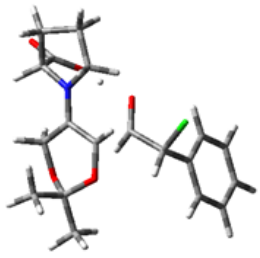
Sum of electronic and zero-point Energies= -1515.715054

Sum of electronic and thermal Energies= -1515.694347

Sum of electronic and thermal Enthalpies= -1515.693467

Sum of electronic and thermal Free Energies= -1515.763081

TS- (*R*)-2-chloro-2-phenylacetaldehyde (*Dudding-Britton model*)



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.415691 (Hartree/Particle)

Thermal correction to Energy= 0.435864

Thermal correction to Enthalpy= 0.436729

Thermal correction to Gibbs Free Energy= 0.367874

Sum of electronic and zero-point Energies= -1628.763872

Sum of electronic and thermal Energies= -1628.743699

Sum of electronic and thermal Enthalpies= -1628.742835

Sum of electronic and thermal Free Energies= -1628.811689

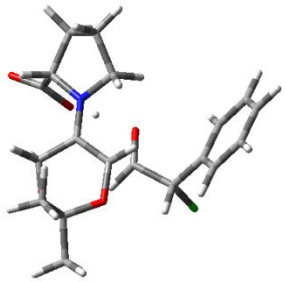
0 1

C	0.50403700	1.11829800	0.95557400
H	0.43369000	0.77800500	1.98374600
C	1.61718800	0.80044100	0.18242600
N	2.37020300	-0.26351100	0.45380200
C	3.44559000	-0.74607700	-0.41488500
H	3.99119500	0.09190000	-0.85580900
C	2.35132800	-0.95917500	1.75620900
H	1.34368400	-1.30112900	1.98839600
H	2.68774300	-0.25965500	2.53155700
C	3.33417500	-2.10951400	1.55561000
H	2.81562900	-2.97500200	1.12915100
H	3.79916900	-2.41496900	2.49490900
C	4.33703000	-1.54572700	0.54755400
H	5.03379100	-0.86169700	1.04186900
H	4.91199500	-2.30802400	0.01987800
C	1.81336000	1.54310300	-1.11259400
H	2.78255300	2.06231000	-1.10625500
H	1.81186300	0.84608500	-1.95635100
O	-0.17952700	2.30382600	0.77011700
O	0.74367200	2.42957300	-1.35145900

C	0.34057700	3.18342600	-0.22708600
C	-0.82287200	4.03860100	-0.68322400
H	-0.48521400	4.77006200	-1.42227400
H	-1.25262100	4.56879200	0.17057200
C	1.48302100	4.00607300	0.36359600
H	2.24748000	3.37569600	0.82753000
H	1.08848400	4.67616200	1.13204400
H	1.95266800	4.60736400	-0.42064400
C	-0.64803100	-0.30610600	0.03706000
H	-0.73307300	0.28616800	-0.89180500
C	-1.91779200	-0.09977500	0.87119500
O	-0.08385600	-1.43807100	0.01757000
C	2.98192800	-1.61540100	-1.60006300
O	1.70897800	-1.91655800	-1.73500600
O	3.81668300	-1.99207400	-2.39783600
H	1.07910800	-1.63996900	-0.97908600
H	-1.59084700	3.40169500	-1.13122300
H	-2.02648200	0.95685000	1.11365600
Cl	-1.78431700	-0.96319900	2.46936600
C	-3.13901800	-0.55947500	0.11033400
C	-3.22387500	-1.84509000	-0.43398500
C	-4.19178800	0.33682900	-0.08254900
C	-4.35136200	-2.22601300	-1.15376200
H	-2.40158500	-2.54054700	-0.29606100
C	-5.31945100	-0.04448100	-0.80664100
H	-4.12847700	1.33735900	0.33780000
C	-5.40142300	-1.32686000	-1.34218500
H	-4.41006300	-3.22583800	-1.57393500
H	-6.13197500	0.66173900	-0.94999700

H -6.28008400 -1.62642800 -1.90609300

TS- (*S*)-2-chloro-2-phenylacetaldehyde (*Polar Felkin-Anh model*)



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.416059 (Hartree/Particle)

Thermal correction to Energy= 0.436183

Thermal correction to Enthalpy= 0.437047

Thermal correction to Gibbs Free Energy= 0.368832

Sum of electronic and zero-point Energies= -1628.763635

Sum of electronic and thermal Energies= -1628.743511

Sum of electronic and thermal Enthalpies= -1628.742647

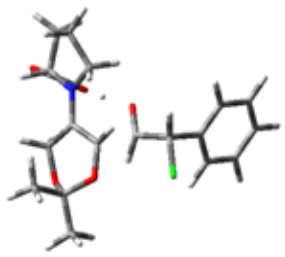
Sum of electronic and thermal Free Energies= -1628.810862

0 1

C	-0.09807000	0.92110500	-0.71887700
H	0.66786000	0.41571000	-1.29792400
C	-1.35611300	0.34049100	-0.57259100
N	-1.52424400	-0.97370000	-0.70481500
C	-2.73919400	-1.69305100	-0.30521100
H	-3.60146300	-1.31330500	-0.86152900
C	-0.58941300	-1.83529700	-1.45524900
H	0.24154400	-2.12509100	-0.80819000
H	-0.19518400	-1.28568700	-2.31431900
C	-1.45718500	-3.02328200	-1.85865500
H	-0.86536700	-3.92786800	-2.01422100
H	-1.99695500	-2.79705900	-2.78414500
C	-2.43405500	-3.15434700	-0.69209500
H	-3.34945900	-3.69425100	-0.93858900
H	-1.94764700	-3.66120400	0.14881300
C	-2.48054800	1.20418100	-0.06870500
H	-3.29144900	1.21399900	-0.81177500
H	-2.89411100	0.81943700	0.86689100
O	0.05815300	2.29182400	-0.75451000
O	-2.02398800	2.50267600	0.23602500
C	-1.14550500	3.05964600	-0.71854700
C	-0.75811100	4.42717200	-0.19679000
H	0.00150300	4.87034200	-0.84610200
C	-1.76058900	3.11819500	-2.11490500
H	-1.89330200	2.12429100	-2.55264500
H	-1.10399300	3.69120200	-2.77494300
H	-2.73453700	3.61453800	-2.07007300

C	0.48676300	0.32108700	1.16700000
H	-0.11371100	1.10167800	1.66389500
C	1.94486300	0.76878000	0.99162500
H	1.95925400	1.78912100	0.61030100
O	0.23573300	-0.90026800	1.37755200
C	-3.10663500	-1.63004000	1.18201800
O	-2.16263900	-1.39592700	2.06827200
O	-4.25353200	-1.86006000	1.50826600
H	-1.22328700	-1.21870700	1.69711900
H	-1.63239100	5.08349200	-0.17616700
Cl	2.62824800	0.92406800	2.69333400
C	2.80943500	-0.12693800	0.14903600
C	3.02125500	-1.47285600	0.46833800
C	3.38664300	0.39619900	-1.01085100
C	3.79150100	-2.27681100	-0.36571200
H	2.57778800	-1.88703900	1.36628900
C	4.15515300	-0.41082000	-1.84744400
H	3.22802500	1.44170900	-1.26352800
C	4.35849200	-1.74959300	-1.52625200
H	3.95054200	-3.32034300	-0.10957200
H	4.59698800	0.01051200	-2.74566100
H	4.96057500	-2.38084700	-2.17339700
H	-0.35367000	4.33322800	0.81485100

TS- (*S*)-2-chloro-2-phenylacetaldehyde *(Evans-Cornforth model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.415013 (Hartree/Particle)

Thermal correction to Energy= 0.435362

Thermal correction to Enthalpy= 0.436227

Thermal correction to Gibbs Free Energy= 0.367091

Sum of electronic and zero-point Energies= -1628.754061

Sum of electronic and thermal Energies= -1628.733711

Sum of electronic and thermal Enthalpies= -1628.732847

Sum of electronic and thermal Free Energies= -1628.801982

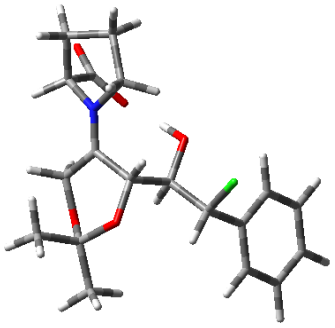
0 1

C	0.75905000	1.12209200	0.82572600
H	0.43358600	0.94701900	1.84687300
C	1.74238300	0.31725700	0.25251200
N	1.96437200	-0.92736600	0.67352100
C	2.83581700	-1.88651900	-0.01699700

H	3.84712500	-1.47686200	-0.10298100
C	1.56271000	-1.41058800	2.00799600
H	0.53351500	-1.77459800	1.96719200
H	1.62340600	-0.59178400	2.72978200
C	2.56306000	-2.52590400	2.29305000
H	2.16785300	-3.25975400	2.99888400
H	3.48466300	-2.10465200	2.70797500
C	2.82435400	-3.11867500	0.91055300
H	3.76117100	-3.67236700	0.83573300
H	2.00296300	-3.78542900	0.62585200
C	2.41572800	0.79901500	-1.00603600
H	3.50446300	0.82674700	-0.84926100
H	2.21750800	0.12068400	-1.83984300
O	0.67047500	2.45773200	0.48536600
O	1.91186600	2.04612900	-1.41951400
C	1.68980700	2.96257600	-0.36773100
C	1.12444800	4.21339200	-1.00867300
H	0.84066100	4.93342500	-0.23688500
H	0.24007900	3.95517700	-1.59776600
C	2.95840500	3.24237400	0.43752100
H	3.28603500	2.36966400	1.01037400
H	2.76679800	4.05458000	1.14370400
H	3.76748900	3.54215800	-0.23515000
C	-0.80468300	0.10638200	-0.11506300
H	-0.73930700	0.78836200	-0.97824600
C	-1.99319600	0.36170600	0.83336400
O	-0.55454300	-1.12885200	-0.23086400
C	2.41266600	-2.31400600	-1.42723200
O	1.15970600	-2.16410300	-1.80165700

O	3.23979500	-2.83734600	-2.14552300
H	0.54217100	-1.71054600	-1.12660900
H	1.87128500	4.67056100	-1.66359800
H	-1.77312100	-0.11426000	1.78956900
Cl	-2.28602200	2.11558200	1.21604000
C	-3.24304300	-0.24036300	0.22970500
C	-3.83273500	-1.35394700	0.82762100
C	-3.78754500	0.27052000	-0.95270200
C	-4.95723200	-1.94771900	0.25638900
H	-3.41118600	-1.76008200	1.74327800
C	-4.90942000	-0.32146900	-1.52219600
H	-3.33663200	1.13904000	-1.42537800
C	-5.49808900	-1.43261800	-0.91838600
H	-5.41014400	-2.81274000	0.73211900
H	-5.32629800	0.08559700	-2.43883200
H	-6.37563100	-1.89281100	-1.36309000

Product- 2-chloro-2-phenylacetaldehyde



%nprocshared=8

%mem=2500MB

opt=calcfc freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.419306 (Hartree/Particle)

Thermal correction to Energy= 0.439499

Thermal correction to Enthalpy= 0.440364

Thermal correction to Gibbs Free Energy= 0.371048

Sum of electronic and zero-point Energies= -1628.788627

Sum of electronic and thermal Energies= -1628.768434

Sum of electronic and thermal Enthalpies= -1628.767569

Sum of electronic and thermal Free Energies= -1628.836885

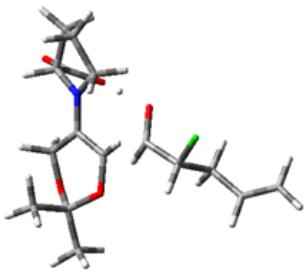
0 1

C	0.38210800	0.92104800	0.82428000
H	0.50333000	0.66496700	1.87868000
C	1.64781900	0.68213000	0.05989300

N	2.50569700	-0.20078900	0.42626500
C	3.55741800	-0.71662900	-0.46210800
H	4.02159500	0.10785500	-1.00811500
C	2.48088900	-0.95570400	1.71124800
H	1.48571700	-1.36545800	1.87250000
H	2.72857900	-0.24597900	2.50509200
C	3.55742600	-2.02539300	1.52936700
H	3.10890700	-2.94127300	1.13167600
H	4.04184600	-2.26178500	2.47848400
C	4.51170900	-1.41718800	0.49860700
H	5.18319300	-0.69142100	0.96931600
H	5.10753600	-2.15879800	-0.03403200
C	1.77812300	1.42102100	-1.23973900
H	2.73287300	1.96379700	-1.27382600
H	1.76245600	0.69866700	-2.06076800
O	-0.07178400	2.25227100	0.78065200
O	0.67245300	2.27054100	-1.42769500
C	0.35009800	3.07714100	-0.31470000
C	-0.85141700	3.90378600	-0.72509400
H	-0.56975800	4.61719800	-1.50448200
H	-1.23358700	4.45437600	0.13819400
C	1.52323800	3.93731400	0.14757900
H	2.33352600	3.33665600	0.57206700
H	1.17813500	4.62405200	0.92502900
H	1.91623100	4.52180600	-0.68956500
C	-0.67425000	-0.05184900	0.18100000
H	-0.82511200	0.28433200	-0.85560500
C	-2.03390100	0.12703600	0.85876700
O	-0.25206900	-1.37643000	0.24341600

C	2.92047000	-1.70837000	-1.52302000
O	1.66373900	-1.72250200	-1.62101000
O	3.75669700	-2.34321800	-2.17207200
H	0.43052100	-1.53219000	-0.45929800
H	-1.63743000	3.24564200	-1.10628500
H	-2.21743400	1.19743500	0.95288100
Cl	-1.96358200	-0.47870400	2.58545200
C	-3.17227400	-0.51677600	0.10832700
C	-3.23212000	-1.89637400	-0.11522700
C	-4.17793100	0.30271300	-0.40869700
C	-4.28217000	-2.44094700	-0.84695000
H	-2.45197700	-2.53715400	0.28035600
C	-5.22761300	-0.24365700	-1.14448400
H	-4.13920000	1.37538100	-0.23569400
C	-5.28201100	-1.61695100	-1.36401900
H	-4.32074000	-3.51327400	-1.01554700
H	-6.00301500	0.40565400	-1.54050100
H	-6.10112500	-2.04638300	-1.93359500

TS- (*R*)-2-chloropent-4-enal (*Dudding-Britton model*)



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.395790 (Hartree/Particle)

Thermal correction to Energy= 0.415286

Thermal correction to Enthalpy= 0.416151

Thermal correction to Gibbs Free Energy= 0.349520

Sum of electronic and zero-point Energies= -1514.473484

Sum of electronic and thermal Energies= -1514.453988

Sum of electronic and thermal Enthalpies= -1514.453123

Sum of electronic and thermal Free Energies= -1514.519754

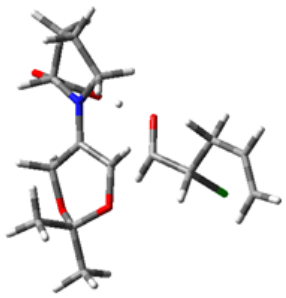
0 1

C	0.16474600	0.82599800	-0.86457400
H	0.47783500	0.29155900	-1.75535900
C	-1.12193700	0.66520200	-0.36009600
N	-1.84402600	-0.41915300	-0.64408400
C	-3.07024100	-0.80034400	0.06503300
H	-3.82422100	-0.01277500	-0.03053000
C	-1.60401700	-1.25990100	-1.83251800
H	-0.82013300	-1.98852200	-1.61405300
H	-1.28193100	-0.62961800	-2.66582400
C	-2.95938100	-1.91668600	-2.07347600
H	-2.86354300	-2.86771800	-2.60172100

H	-3.60000400	-1.25279300	-2.66328900
C	-3.52045000	-2.08370800	-0.66275300
H	-4.60495900	-2.19663200	-0.62697900
H	-3.06544700	-2.95616500	-0.18064000
C	-1.60634300	1.64614600	0.67376400
H	-2.52061200	2.13794800	0.31098000
H	-1.85000800	1.14650200	1.61510200
O	0.84797200	2.01639600	-0.71872400
O	-0.59820900	2.57640500	1.00040900
C	0.12188000	3.08094900	-0.10480000
C	1.15763000	4.02998800	0.46046200
H	0.66769900	4.89705100	0.91157700
H	1.82368300	4.37313900	-0.33549100
C	-0.78481900	3.74712700	-1.13726300
H	-1.43718200	3.02730900	-1.64014700
H	-0.16946500	4.23207800	-1.89967400
H	-1.40747400	4.50408500	-0.65120300
C	0.96646400	-0.45889200	0.52673600
H	0.86291700	0.27761200	1.34479600
C	2.40765800	-0.44269800	0.01677600
O	0.33696500	-1.55442400	0.57749100
C	-2.91957100	-1.09377100	1.56159900
O	-1.74508200	-1.45847900	2.02876200
O	-3.90592700	-1.04117300	2.26859300
H	-0.96900100	-1.48398500	1.35544900
H	1.74832000	3.51435800	1.22283400
C	3.33787400	-0.98547700	1.10778400
H	3.10032100	-0.41993500	2.02025500
C	4.79425600	-0.80938500	0.79044300

H	2.69430000	0.57504300	-0.25312100
Cl	2.57838900	-1.43300300	-1.49560400
H	3.09916800	-2.03642300	1.30226300
C	5.68373800	-1.79789100	0.74422700
H	6.73135100	-1.60949400	0.52304300
H	5.39842700	-2.83189600	0.93007500
H	5.11484400	0.21464700	0.59520300

TS- (*S*)-2-chloropent-4-enal (*Polar Felkin-Anh model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.396046 (Hartree/Particle)

Thermal correction to Energy= 0.415357

Thermal correction to Enthalpy= 0.416221

Thermal correction to Gibbs Free Energy= 0.350298

Sum of electronic and zero-point Energies= -1514.472342

Sum of electronic and thermal Energies= -1514.453031

Sum of electronic and thermal Enthalpies= -1514.452167

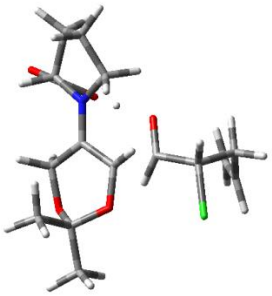
Sum of electronic and thermal Free Energies= -1514.518090

0 1

C	0.37552700	0.67318500	-0.81041600
H	0.71810000	0.05855700	-1.63681900
C	-0.97564100	0.67719700	-0.46050100
N	-1.76422600	-0.35434500	-0.74931100
C	-3.10289400	-0.54999100	-0.17930800
H	-3.74081200	0.30520000	-0.42235700
C	-1.47540600	-1.32118600	-1.82600900
H	-0.82460100	-2.11029100	-1.44255900
H	-0.97102600	-0.81180500	-2.65117800
C	-2.85854400	-1.83958000	-2.20613100
H	-2.81258400	-2.83307900	-2.65705000
H	-3.33188800	-1.15474900	-2.91753300
C	-3.61034000	-1.82900300	-0.87656200
H	-4.69588000	-1.81272900	-0.98284600
H	-3.33305800	-2.70711700	-0.28245700
C	-1.47039200	1.77723200	0.44046900
H	-2.29653200	2.31048400	-0.05257500
H	-1.85252700	1.37575800	1.38292600
O	1.14771500	1.80991800	-0.67412600
O	-0.42231900	2.64561100	0.80574700
C	0.45795400	2.98372900	-0.24517400

C	1.50516800	3.89808400	0.35413700
H	1.04303600	4.83560700	0.67477600
H	2.27591500	4.11898400	-0.38875000
C	-0.26409100	3.61950400	-1.43110600
H	-0.92056600	2.91121600	-1.94524500
H	0.47466400	3.97832600	-2.15263500
H	-0.86480000	4.46745900	-1.08906300
C	0.87395000	-0.53613900	0.75502500
H	0.78018600	0.28085500	1.48968300
C	2.32725200	-0.75708600	0.32469600
H	2.74368800	0.16101300	-0.08888800
O	0.11744900	-1.55183000	0.83707700
C	-3.17161200	-0.73938100	1.34070600
O	-2.10633400	-1.15693700	1.98757500
O	-4.23427400	-0.55172000	1.89848700
H	-1.25002500	-1.29902200	1.43282500
H	1.96809300	3.41161600	1.21714500
C	2.49979300	-1.94976600	-0.59772100
H	1.73944400	-1.86816800	-1.38721300
C	3.84127400	-2.11237900	-1.25786800
Cl	3.27487000	-1.01506400	1.87827700
H	2.23898400	-2.86405500	-0.05377100
C	4.87734700	-1.27786400	-1.21238100
H	4.86740800	-0.35087000	-0.64358300
H	5.79462300	-1.50099200	-1.75142000
H	3.93297900	-3.02536600	-1.84617000

TS- (*S*)-2-chloropent-4-enal *(Evans-Cornforth model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.395632 (Hartree/Particle)

Thermal correction to Energy= 0.415037

Thermal correction to Enthalpy= 0.415901

Thermal correction to Gibbs Free Energy= 0.349296

Sum of electronic and zero-point Energies= -1514.466776

Sum of electronic and thermal Energies= -1514.447371

Sum of electronic and thermal Enthalpies= -1514.446506

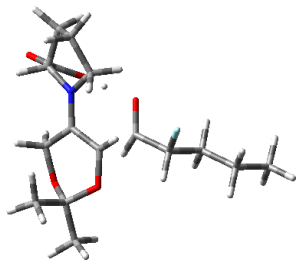
Sum of electronic and thermal Free Energies= -1514.513112

0 1

C	-0.38619400	0.95766700	0.85306100
H	-0.51792800	0.67913800	1.89478200
C	0.87596500	0.86988900	0.26114100
N	1.80562300	0.03296300	0.71569800
C	3.05061200	-0.27741400	0.00069600
H	3.61510300	0.64282500	-0.17875400
C	1.81341500	-0.50214500	2.09052500
H	1.20902600	-1.41092200	2.12958400
H	1.39083500	0.23854900	2.77424800
C	3.29080600	-0.77744100	2.34986100
H	3.43499100	-1.54886700	3.10944900
H	3.79073400	0.13814400	2.68237900
C	3.80934500	-1.19957300	0.97666400
H	4.88809400	-1.09090900	0.85729600
H	3.54241400	-2.24393300	0.78062700
C	1.09914100	1.58194100	-1.04711800
H	1.96561100	2.25381100	-0.95529400
H	1.31456600	0.86911400	-1.84758900
O	-1.24982100	1.97314000	0.49193700
O	-0.05625400	2.26792300	-1.46560600
C	-0.74812700	2.93304100	-0.42889900
C	-1.95869800	3.57593500	-1.07348500
H	-2.59199600	4.03068600	-0.30742600
H	-2.53516700	2.81589700	-1.60784700

C	0.13096500	3.94866600	0.30072900
H	0.92611300	3.47019900	0.88032400
H	-0.48642200	4.52884700	0.99183100
H	0.58818000	4.63252300	-0.42076500
C	-1.04425500	-0.82271400	0.02269300
H	-1.34438500	-0.31966200	-0.91022200
C	-2.20497300	-1.20602900	0.95458400
O	-0.11618800	-1.68996700	0.02288800
C	2.90737500	-0.97910200	-1.35558000
O	1.79691800	-1.62570700	-1.63446600
O	3.85433200	-0.96473400	-2.11599600
H	1.05772700	-1.58535400	-0.92226400
H	-1.64243000	4.34942900	-1.77858600
C	-2.73880900	-2.59911000	0.58410800
H	-1.90377000	-3.29142600	0.72560600
C	-3.26834400	-2.70926900	-0.81967100
H	-1.85407400	-1.22475100	1.98758700
Cl	-3.56967100	-0.00599900	0.92211300
H	-3.52065300	-2.86438300	1.30517200
C	-2.64942000	-3.36005600	-1.80246400
H	-1.69824700	-3.86412200	-1.64259000
H	-3.07228100	-3.41345600	-2.80278400
H	-4.21570000	-2.21107900	-1.02169100

TS- (*R*)-2-fluoreo pentanal (*Dudding-Britton model*)



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.420543 (Hartree/Particle)

Thermal correction to Energy= 0.440197

Thermal correction to Enthalpy= 0.441062

Thermal correction to Gibbs Free Energy= 0.374549

Sum of electronic and zero-point Energies= -1155.313185

Sum of electronic and thermal Energies= -1155.293530

Sum of electronic and thermal Enthalpies= -1155.292666

Sum of electronic and thermal Free Energies= -1155.359179

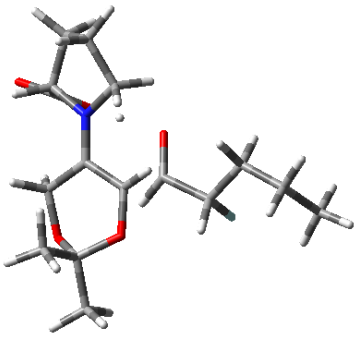
0 1

C	-0.17805900	0.88434200	0.86624800
H	-0.51007200	0.40732100	1.78146400

C	1.09029100	0.63040800	0.35374000
N	1.74919600	-0.48181300	0.67741900
C	2.93739400	-0.97560600	-0.02556700
H	3.75035800	-0.24690500	0.05079100
C	1.45899300	-1.25691500	1.89862400
H	0.60534900	-1.91442400	1.71985700
H	1.21210800	-0.57020200	2.71312700
C	2.75501300	-2.02341700	2.14314600
H	2.58367800	-2.94982300	2.69559800
H	3.45606600	-1.40327000	2.71130000
C	3.28729600	-2.27187000	0.73301600
H	4.35879700	-2.47343600	0.69344500
H	2.75876800	-3.11624100	0.27654800
C	1.61376300	1.53824700	-0.72654100
H	2.55446900	1.99983300	-0.39243800
H	1.82291900	0.98748600	-1.64683600
O	-0.79996200	2.10129600	0.67099500
O	0.65094800	2.50256200	-1.08833700
C	-0.02806400	3.09549900	-0.00152300
C	-1.02051700	4.06954400	-0.60163500
H	-0.49194800	4.88733500	-1.09906800
H	-1.65827200	4.48486400	0.18303800
C	0.92620600	3.76286200	0.98666000
H	1.53302400	3.03452300	1.53253300
H	0.34922800	4.33448000	1.71850900
H	1.59397100	4.44584200	0.45310900
C	-1.07907900	-0.42210000	-0.42033700
H	-1.03686900	0.28377500	-1.26850800
C	-2.43717900	-0.40420500	0.27009600

O	-0.47286700	-1.53661700	-0.48662200
C	2.76154100	-1.29035100	-1.51605300
O	1.56359300	-1.57397700	-1.97537000
O	3.75010300	-1.32292800	-2.22238800
H	0.78310500	-1.54022700	-1.29621500
H	-1.64629600	3.54942400	-1.33215900
C	-3.48051000	-1.13560000	-0.55987500
H	-3.52703300	-0.65514000	-1.54586100
C	-4.86572700	-1.12872400	0.08773100
H	-4.79942500	-1.59509500	1.07719100
H	-5.18240600	-0.08984000	0.24968900
H	-2.75061900	0.62604500	0.46517800
H	-3.13426700	-2.16433100	-0.71732400
C	-5.90846600	-1.85811000	-0.75548300
H	-5.62475300	-2.90493300	-0.91689200
H	-6.88828300	-1.84898800	-0.26558900
H	-6.02139000	-1.38746100	-1.73953400
F	-2.31849700	-1.05051400	1.50860100

TS- (*S*)-2-fluoreo pentanal (*Polar Felkin-Anh model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.421391 (Hartree/Particle)

Thermal correction to Energy= 0.440825

Thermal correction to Enthalpy= 0.441689

Thermal correction to Gibbs Free Energy= 0.375985

Sum of electronic and zero-point Energies= -1155.309404

Sum of electronic and thermal Energies= -1155.289970

Sum of electronic and thermal Enthalpies= -1155.289106

Sum of electronic and thermal Free Energies= -1155.354810

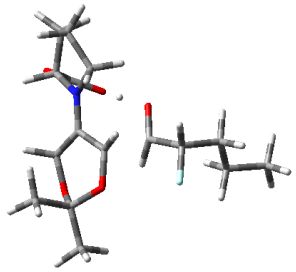
0 1

C	-0.43022900	0.72227100	0.76397700
H	-0.84619100	0.12030200	1.56570000
C	0.92024900	0.62621600	0.44010900
N	1.62706300	-0.46403900	0.73750400
C	2.95633900	-0.75638100	0.18899700
H	3.65800000	0.03992000	0.45584900
C	1.25130300	-1.40267300	1.81155000
H	0.53848000	-2.13519700	1.42580100
H	0.78555700	-0.85142400	2.63302000
C	2.58320600	-2.03605300	2.20045100
H	2.45204000	-3.02474700	2.64546200

H	3.10675000	-1.39654500	2.91875800
C	3.34499800	-2.08028200	0.87740400
H	4.42675700	-2.16143300	0.99239700
H	2.99658900	-2.92492600	0.27236400
C	1.51713100	1.69362500	-0.43753500
H	2.36790800	2.16024600	0.08058700
H	1.89227900	1.27312000	-1.37435800
O	-1.11593200	1.91056000	0.61328700
O	0.54693100	2.64150300	-0.82062800
C	-0.33398100	3.03444300	0.21037400
C	-1.30053300	4.02283700	-0.40728700
H	-0.76849000	4.92964000	-0.70738900
H	-2.07380500	4.28948100	0.31768400
C	0.40075400	3.61203600	1.41851800
H	0.98712500	2.85511000	1.94784700
H	-0.32787500	4.02415900	2.12180300
H	1.07358000	4.41241500	1.09660100
C	-0.96740000	-0.46889300	-0.82785500
H	-0.77982400	0.32455100	-1.57234200
C	-2.45324500	-0.55978800	-0.47550300
H	-2.81630000	0.39530800	-0.08572700
O	-0.29014500	-1.54056900	-0.86842600
C	3.03881300	-0.93089000	-1.33207100
O	1.96190700	-1.28625600	-1.99678800
O	4.11738100	-0.79337400	-1.87439200
H	1.09185900	-1.38185600	-1.45128100
H	-1.77225700	3.57523700	-1.28625700
C	-2.80588900	-1.71802800	0.43666200
H	-2.10554600	-1.70752100	1.28020600

C	-4.23893400	-1.68864800	0.97831900
H	-4.39919100	-0.74462500	1.51646600
H	-4.33600900	-2.48817300	1.72329000
H	-2.61632000	-2.64977900	-0.10803400
C	-5.32685800	-1.86297300	-0.08125100
H	-5.17084200	-2.78661300	-0.65157800
H	-6.31603300	-1.92168500	0.38627600
H	-5.33693700	-1.03217800	-0.79203400
F	-3.08846800	-0.73781700	-1.72524700

TS- (*S*)-2-fluoreo pentanal *(Evans-Cornforth model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.420766 (Hartree/Particle)

Thermal correction to Energy= 0.440341

Thermal correction to Enthalpy= 0.441206

Thermal correction to Gibbs Free Energy= 0.374776

Sum of electronic and zero-point Energies= -1155.308728

Sum of electronic and thermal Energies= -1155.289152

Sum of electronic and thermal Enthalpies= -1155.288287

Sum of electronic and thermal Free Energies= -1155.354718

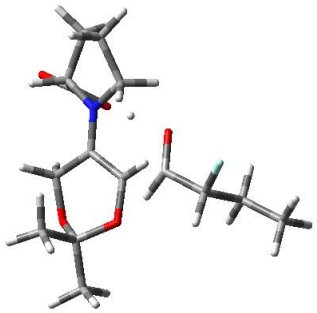
0 1

C	-0.16823600	1.01085300	0.93043800
H	-0.28971700	0.73278000	1.97307800
C	1.01462600	0.70263600	0.25696500
N	1.79252400	-0.30716100	0.64176100
C	2.89359800	-0.85286400	-0.16121300
H	3.63201300	-0.07119000	-0.36460700
C	1.77440000	-0.86661100	2.00640700
H	0.99004300	-1.62325600	2.07810700
H	1.57090200	-0.07008100	2.72687800
C	3.17029900	-1.46187300	2.15778300
H	3.19360500	-2.26677300	2.89553500
H	3.87859000	-0.68577700	2.46606200
C	3.49321400	-1.94615700	0.74599200
H	4.55938300	-2.07438500	0.55417700
H	2.98930700	-2.89990900	0.55394600
C	1.29486700	1.40032000	-1.04761500
H	2.27952500	1.88828200	-0.99299800
H	1.32085200	0.68794900	-1.87656800
O	-0.85588200	2.17179100	0.63423400

O	0.27350000	2.31190100	-1.37707000
C	-0.22361700	3.05564300	-0.28301700
C	-1.31823500	3.94438100	-0.83668300
H	-1.81213700	4.47865100	-0.02077200
H	-2.05682200	3.33056100	-1.35945300
C	0.87263500	3.85201200	0.42428800
H	1.58303700	3.20592600	0.94856200
H	0.41627600	4.51660000	1.16280000
H	1.42249600	4.45761700	-0.30244300
C	-1.18943300	-0.57077900	0.10807500
H	-1.40541100	-0.00188100	-0.81185300
C	-2.35949900	-0.65043600	1.08664400
O	-0.48236200	-1.62894700	0.06031400
C	2.51619600	-1.46510400	-1.51607000
O	1.28236000	-1.86508400	-1.72364600
O	3.39247000	-1.61157500	-2.34540100
H	0.61156600	-1.71893800	-0.95027900
H	-0.89702800	4.67284400	-1.53488700
C	-3.35181900	-1.73656200	0.68634000
H	-2.83034300	-2.69810800	0.74835800
C	-3.96842400	-1.55895600	-0.70235600
H	-4.39552300	-0.55249700	-0.78351800
H	-3.18592600	-1.63410000	-1.46767000
H	-1.97289500	-0.85678700	2.09031900
H	-4.14605600	-1.75013800	1.44368600
C	-5.04982400	-2.60084400	-0.97934600
H	-4.63864600	-3.61640200	-0.93079100
H	-5.85792200	-2.53360500	-0.24097700
H	-5.49045300	-2.46422400	-1.97307800

F -3.03350800 0.57092600 1.13653500

TS- (*R*)- 2-fluoreo butanal (*Dudding-Britton model*)



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.392374 (Hartree/Particle)

Thermal correction to Energy= 0.410705

Thermal correction to Enthalpy= 0.411569

Thermal correction to Gibbs Free Energy= 0.348641

Sum of electronic and zero-point Energies= -1116.037387

Sum of electronic and thermal Energies= -1116.019056

Sum of electronic and thermal Enthalpies= -1116.018192

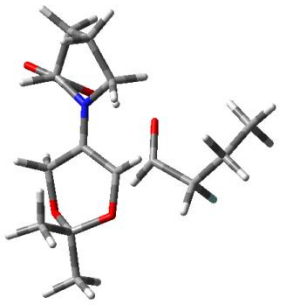
Sum of electronic and thermal Free Energies= -1116.081120

0 1

C	-0.73251000	0.54547300	0.84584300
H	-0.92455200	-0.06879900	1.71828900
C	0.56610600	0.75562400	0.39382300
N	1.54792100	-0.08929600	0.70922600
C	2.85973200	-0.11933600	0.05402200
H	3.37516000	0.83558300	0.19695900
C	1.48979900	-0.97846900	1.88434400
H	0.92099600	-1.87726800	1.63482900
H	0.98967900	-0.46036600	2.70748600
C	2.95811700	-1.27135000	2.17441600
H	3.09132400	-2.22594800	2.68812100
H	3.38269300	-0.47756200	2.79776800
C	3.59861000	-1.25715000	0.78764100
H	4.67564200	-1.08325300	0.79954400
H	3.40645400	-2.20752800	0.27713300
C	0.79404400	1.83687000	-0.62808600
H	1.51775600	2.56731500	-0.23743600
H	1.20487500	1.42789000	-1.55468500
O	-1.71780700	1.49494500	0.66556500
O	-0.42194200	2.44470900	-1.00218700
C	-1.29983000	2.72197800	0.06835000
C	-2.53858400	3.33744200	-0.54811800
H	-2.29528400	4.30554500	-0.99410800
H	-3.30437800	3.48323400	0.21829900

C	-0.66448000	3.62034200	1.12760400
H	0.14475900	3.11745100	1.66542700
H	-1.42373000	3.91133500	1.85830900
H	-0.26280300	4.52279100	0.65724500
C	-1.08391700	-0.90985100	-0.55490500
H	-1.22319700	-0.18003000	-1.37205000
C	-2.41254200	-1.37464700	0.02701400
O	-0.14188100	-1.75932800	-0.61223400
C	2.86191400	-0.40422800	-1.45298400
O	1.84915800	-1.04944700	-1.98638300
O	3.83355700	-0.07404600	-2.10415800
H	1.07595300	-1.30909800	-1.34938100
H	-2.93032300	2.67275900	-1.32296300
C	-3.09752000	-2.35158300	-0.91727200
H	-3.23067600	-1.84957700	-1.88325800
C	-4.44379400	-2.83660200	-0.38642200
H	-4.32450200	-3.34237300	0.57683600
H	-5.13826000	-1.99980100	-0.24733500
H	-4.90283400	-3.54347900	-1.08530600
H	-3.05960200	-0.51676700	0.23538800
H	-2.41842600	-3.19574500	-1.08227600
F	-2.16908100	-2.02477500	1.24401600

TS- (*S*)- 2-fluoreo butanal (*Polar Felkin-Anh model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.392360 (Hartree/Particle)

Thermal correction to Energy= 0.410790

Thermal correction to Enthalpy= 0.411654

Thermal correction to Gibbs Free Energy= 0.348219

Sum of electronic and zero-point Energies= -1116.033025

Sum of electronic and thermal Energies= -1116.014595

Sum of electronic and thermal Enthalpies= -1116.013731

Sum of electronic and thermal Free Energies= -1116.077167

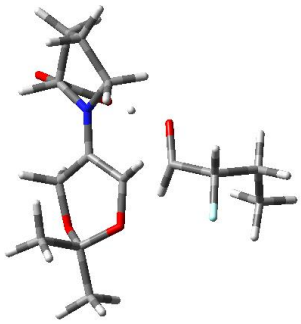
0 1

C	0.96319500	-0.34436400	0.80824100
H	1.02941200	0.31321200	1.66954400
C	-0.27292900	-0.84100700	0.40166800

N	-1.40578200	-0.20943500	0.70555500
C	-2.70286900	-0.51200900	0.08971700
H	-2.96355100	-1.56120800	0.25993300
C	-1.53745000	0.71721300	1.84595500
H	-1.23866500	1.72167100	1.53763800
H	-0.88969700	0.38679100	2.66207500
C	-3.02048600	0.63279700	2.19158100
H	-3.37528000	1.53410600	2.69576200
H	-3.20616900	-0.22754900	2.84296200
C	-3.68157000	0.42191500	0.83065700
H	-4.67741300	-0.01976000	0.88701900
H	-3.75511400	1.37643600	0.29783400
C	-0.29300100	-1.99800600	-0.56142600
H	-0.87077000	-2.82624100	-0.12537500
H	-0.77154200	-1.72080600	-1.50466000
O	2.11435800	-1.09123600	0.65044000
O	1.01327300	-2.39423800	-0.91173500
C	1.92991200	-2.41905400	0.16199500
C	3.25918500	-2.84640300	-0.42376100
H	3.19054700	-3.87109500	-0.79894600
H	4.03712000	-2.80061200	0.34266200
C	1.47174600	-3.32834400	1.30085800
H	0.58038700	-2.94274500	1.80467700
H	2.26994600	-3.40715000	2.04365700
H	1.25007000	-4.32681500	0.91262500
C	0.97629600	1.08574400	-0.66638000
H	1.20855800	0.35837300	-1.46449500
C	2.24591800	1.79668400	-0.18960400
H	2.95909100	1.05720300	0.18213500

O	-0.11996000	1.72402200	-0.70344800
C	-2.80672300	-0.26586500	-1.42022300
O	-1.97220600	0.57284000	-1.99278500
O	-3.69886400	-0.81285300	-2.03735000
H	-1.25753900	1.00173800	-1.38655200
H	3.52820200	-2.17957500	-1.24749800
C	2.04073000	2.91854900	0.82001900
H	1.37811900	2.54745700	1.61063000
C	1.47635100	4.20947200	0.22849800
H	1.36556000	4.96669500	1.01218400
H	2.14882800	4.61401100	-0.53394200
H	0.50048400	4.03646000	-0.23023300
H	3.00620300	3.12862400	1.29437700
F	2.82345000	2.32829200	-1.36118200

TS- (*S*)- 2-fluoreo butanal *(Evans-Cornforth model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.391838 (Hartree/Particle)

Thermal correction to Energy= 0.410197

Thermal correction to Enthalpy= 0.411062

Thermal correction to Gibbs Free Energy= 0.347707

Sum of electronic and zero-point Energies= -1116.033454

Sum of electronic and thermal Energies= -1116.015095

Sum of electronic and thermal Enthalpies= -1116.014230

Sum of electronic and thermal Free Energies= -1116.077585

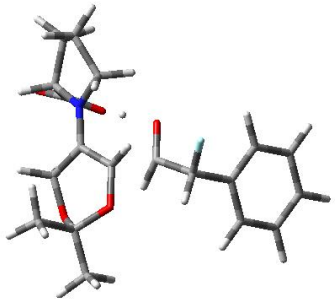
0 1

C	-0.78457700	0.52532000	0.90394700
H	-0.83646700	0.10533800	1.90393400
C	0.45322600	0.79767100	0.32069800
N	1.55617200	0.14928500	0.68981800
C	2.82498800	0.19217100	-0.04716200
H	3.19284700	1.22152000	-0.10135000
C	1.69752200	-0.52268300	1.99515600
H	1.28048700	-1.53006800	1.93179600
H	1.15470400	0.04193200	2.75790500
C	3.20558200	-0.53014700	2.22198000
H	3.51571600	-1.33964900	2.88620800
H	3.52418800	0.42145700	2.66013500
C	3.76632600	-0.67840600	0.80934100
H	4.80290600	-0.35448600	0.70620300
H	3.69489200	-1.72303900	0.48638000

C	0.49259500	1.69549100	-0.88786300
H	1.20193200	2.51678900	-0.70531700
H	0.83717700	1.14966800	-1.77058300
O	-1.87200800	1.33368500	0.63277900
O	-0.78779000	2.17301700	-1.22568800
C	-1.59922600	2.50952300	-0.11853200
C	-2.92541900	2.96698200	-0.68971500
H	-3.64074300	3.14111000	0.11828100
H	-3.32202400	2.19792500	-1.35824500
C	-0.95410400	3.56881500	0.77519400
H	-0.06526700	3.19132400	1.28971700
H	-1.67333500	3.88710300	1.53457300
H	-0.66657700	4.43794100	0.17584200
C	-1.01916600	-1.23367000	-0.13624400
H	-1.41726300	-0.69735700	-1.01355400
C	-2.08181400	-1.90133000	0.73336800
O	0.06407000	-1.89718500	-0.22300500
C	2.80182400	-0.34332000	-1.48423500
O	1.85669600	-1.18107600	-1.84631700
O	3.69959600	-0.01661900	-2.23535900
H	1.14666700	-1.41275800	-1.13203900
H	-2.79160300	3.89632900	-1.24999700
C	-2.56698300	-3.21038100	0.11718600
H	-1.71470700	-3.89686500	0.08655000
C	-3.17697100	-3.05169100	-1.27438900
H	-3.97552800	-2.30292400	-1.26905400
H	-2.42642400	-2.74293100	-2.00996200
H	-1.65753300	-2.09169000	1.72492200
H	-3.30499200	-3.63978100	0.80491400

H	-3.60534700	-3.99949700	-1.61566500
F	-3.18158300	-1.05811400	0.89755900

TS- (*R*)-2-fluoreo phenylacetaldehyde (*Dudding-Britton model*)



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.416895 (Hartree/Particle)

Thermal correction to Energy= 0.436828

Thermal correction to Enthalpy= 0.437693

Thermal correction to Gibbs Free Energy= 0.369701

Sum of electronic and zero-point Energies= -1268.383949

Sum of electronic and thermal Energies= -1268.364015

Sum of electronic and thermal Enthalpies= -1268.363151

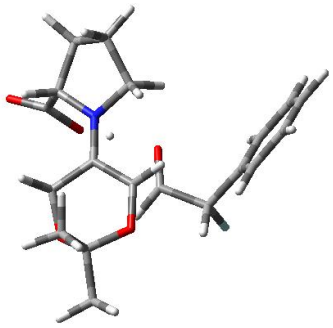
Sum of electronic and thermal Free Energies= -1268.431143

0 1

C	0.58024000	1.08142500	0.97205400
H	0.35783800	0.73939700	1.97670400
C	1.63026800	0.52912400	0.24840200
N	2.11891800	-0.67383900	0.55466200
C	3.01007800	-1.45011500	-0.31238100
H	3.94180300	-0.90317000	-0.48771000
C	1.96802500	-1.28288800	1.88954300
H	0.99191100	-1.76760900	1.96405800
H	2.03438000	-0.50289300	2.65340500
C	3.12427100	-2.27604900	1.95326200
H	2.91507400	-3.10324600	2.63492000
H	4.03580100	-1.77074700	2.28876200
C	3.27335900	-2.73255900	0.50294700
H	4.25231300	-3.15361900	0.26971100
H	2.50880100	-3.48081500	0.26576700
C	2.07587000	1.23240000	-1.00534700
H	3.14116700	1.49251300	-0.91985400
H	1.96038200	0.59289000	-1.88444700
O	0.17846700	2.38601900	0.77439800
O	1.27414300	2.36279800	-1.26528900
C	0.97406100	3.14996300	-0.13229100
C	0.09244600	4.27976400	-0.62140300
H	0.65478600	4.92660700	-1.30007600
H	-0.25633900	4.87467500	0.22678200
C	2.22835800	3.65000300	0.58168500
H	2.78166700	2.83721500	1.06125400
H	1.94147700	4.36473200	1.35751000
H	2.88898600	4.15033800	-0.13251000
C	-0.81528900	-0.09916200	0.01249900

H	-0.79414600	0.50107200	-0.91399400
C	-1.98265600	0.29796600	0.91813100
O	-0.47043700	-1.31685800	-0.00086500
C	2.45478100	-1.83161900	-1.68946700
O	1.15244100	-1.90495100	-1.85853700
O	3.23646600	-2.11610300	-2.57482700
H	0.56981000	-1.66179100	-1.04623100
H	-0.77196600	3.86775000	-1.14934400
H	-2.00956000	1.38327500	1.04528700
C	-3.27678500	-0.20203400	0.32611300
C	-3.66045200	-1.53346800	0.50260700
C	-4.06960600	0.64740800	-0.44567600
C	-4.83355900	-2.00456000	-0.07735000
H	-3.03785200	-2.19488600	1.09564400
C	-5.23955200	0.17144200	-1.03501400
H	-3.77381300	1.68464100	-0.58395600
C	-5.62485700	-1.15410100	-0.84958700
H	-5.12885200	-3.03957600	0.06931200
H	-5.85267000	0.83881800	-1.63370900
H	-6.53905700	-1.52503600	-1.30394000
F	-1.78522400	-0.28428000	2.17029300

TS- (*S*)-2-fluoreo phenylacetaldehyde (*Polar Felkin-Anh model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.417132 (Hartree/Particle)

Thermal correction to Energy= 0.437030

Thermal correction to Enthalpy= 0.437895

Thermal correction to Gibbs Free Energy= 0.370269

Sum of electronic and zero-point Energies= -1268.383250

Sum of electronic and thermal Energies= -1268.363352

Sum of electronic and thermal Enthalpies= -1268.362487

Sum of electronic and thermal Free Energies= -1268.430114

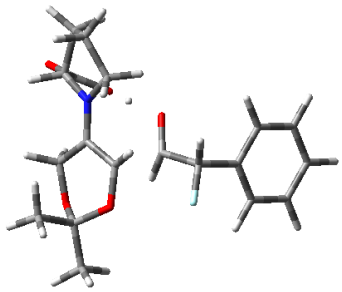
0 1

C	-0.19035500	1.05385900	-0.60384400
H	0.68177900	0.76100800	-1.17854500

C	-1.29293200	0.21363200	-0.52091800
N	-1.17696200	-1.09953800	-0.73423800
C	-2.22535100	-2.07992400	-0.43358400
H	-3.13636500	-1.84446300	-0.99261400
C	-0.06672300	-1.69125000	-1.50434300
H	0.78983000	-1.85602200	-0.84613400
H	0.22878800	-1.00759400	-2.30488700
C	-0.65984200	-2.99528900	-2.02769300
H	0.10966700	-3.74496200	-2.22378900
H	-1.21118100	-2.81104500	-2.95566500
C	-1.61754600	-3.41392000	-0.91384200
H	-2.39597700	-4.10682800	-1.23641000
H	-1.05876000	-3.87792400	-0.09332700
C	-2.57914700	0.78291300	0.01524600
H	-3.37156900	0.68098100	-0.74065400
H	-2.90649200	0.25220400	0.91281700
O	-0.32029300	2.42490200	-0.53430900
O	-2.40696000	2.12183800	0.42332200
C	-1.65821200	2.92068700	-0.46773200
C	-1.56869200	4.29373100	0.16442200
H	-0.92316400	4.93953400	-0.43654400
C	-2.26257000	2.95584500	-1.86973200
H	-2.17904100	1.99117200	-2.37893200
H	-1.73571200	3.70032500	-2.47246700
H	-3.31981300	3.23155400	-1.81200900
C	0.48537900	0.44052000	1.27772700
H	-0.26437900	1.05650600	1.80289500
C	1.83622000	1.16486900	1.18789300
H	1.69412300	2.17211200	0.78945600

O	0.47469800	-0.81492300	1.40540100
C	-2.63273600	-2.21172500	1.03805000
O	-1.78303100	-1.84915700	1.97554600
O	-3.71037000	-2.70507300	1.30277600
H	-0.89682600	-1.45171100	1.65238300
H	-2.56262100	4.74493600	0.22608500
C	2.89865000	0.41918500	0.43110300
C	3.45885100	-0.74686300	0.96133800
C	3.32255900	0.87384000	-0.81842900
C	4.41923800	-1.45110800	0.24262000
H	3.13654000	-1.10171400	1.93408300
C	4.27914800	0.16408900	-1.54258700
H	2.90241000	1.78965000	-1.22801300
C	4.82874000	-1.00013300	-1.01253800
H	4.85019300	-2.35562400	0.66232200
H	4.60074400	0.52778700	-2.51426600
H	-1.15062600	4.20652000	1.17107500
H	5.57796000	-1.55307400	-1.57194600
F	2.23320200	1.30833200	2.53043600

TS- (*S*)-2-fluoreo phenylacetaldehyde *(Evans-Cornforth model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.416980 (Hartree/Particle)

Thermal correction to Energy= 0.436829

Thermal correction to Enthalpy= 0.437694

Thermal correction to Gibbs Free Energy= 0.370045

Sum of electronic and zero-point Energies= -1268.379792

Sum of electronic and thermal Energies= -1268.359943

Sum of electronic and thermal Enthalpies= -1268.359079

Sum of electronic and thermal Free Energies= -1268.426728

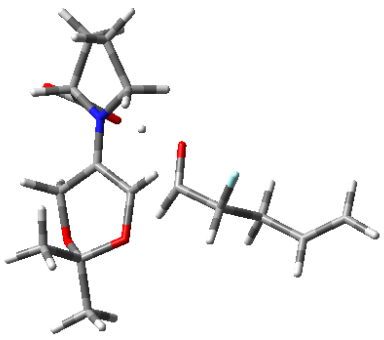
0 1

C	-0.63647800	1.11477000	-0.91791300
H	-0.37067200	0.87206500	-1.94220500
C	-1.64646500	0.40670600	-0.26901100

N	-1.97341200	-0.83396000	-0.63081400
C	-2.84453000	-1.71783900	0.15276300
H	-3.83013700	-1.25872800	0.27834400
C	-1.67701100	-1.39008800	-1.96407700
H	-0.66390100	-1.79793500	-1.97092900
H	-1.74873900	-0.59977100	-2.71625500
C	-2.73825800	-2.47194300	-2.13666000
H	-2.41620100	-3.25354800	-2.82811600
H	-3.66581300	-2.03106900	-2.51639200
C	-2.93943000	-2.98985700	-0.71413800
H	-3.89134700	-3.49987100	-0.55903200
H	-2.12975400	-3.67777700	-0.44665200
C	-2.23231500	0.98845200	0.99042900
H	-3.32287700	1.07892600	0.87494600
H	-2.04187900	0.33986900	1.84962200
O	-0.43326400	2.45268900	-0.64150600
O	-1.63541800	2.22054900	1.31838500
C	-1.39063100	3.06578800	0.21268600
C	-0.72892400	4.30898700	0.76990200
H	-0.42664800	4.96989300	-0.04680300
H	0.15648400	4.02648200	1.34613700
C	-2.66492000	3.38584500	-0.56848800
H	-3.06902600	2.50785700	-1.08102900
H	-2.44439100	4.14409600	-1.32447600
H	-3.42901100	3.77572500	0.11065300
C	0.87383200	0.03205800	0.00264000
H	0.85175000	0.68705900	0.89046100
C	2.02103700	0.34319000	-0.96704500
O	0.59126700	-1.20070700	0.09601500

C	-2.35293000	-2.09719500	1.55488800
O	-1.06884800	-2.02376900	1.82983900
O	-3.16182300	-2.51344800	2.35978200
H	-0.46393800	-1.66521900	1.08192500
H	-1.42494400	4.84594500	1.42008300
H	1.80801600	-0.14027400	-1.92559200
C	3.32132900	-0.17095500	-0.39243700
C	3.68497900	-1.50541700	-0.58276200
C	4.14079400	0.66435800	0.36771400
C	4.85930500	-1.99921900	-0.02302400
H	3.04419000	-2.15672700	-1.17012200
C	5.31808900	0.16937600	0.92498400
H	3.86331600	1.70291600	0.51697600
C	5.67970400	-1.16198200	0.73224800
H	5.13571000	-3.03792500	-0.17988000
H	5.95299100	0.82633900	1.51258400
H	6.59778700	-1.54674400	1.16687600
F	2.12494800	1.71037900	-1.18463800

TS-(*R*)- 2-fluoreopent-4-enal (*Dudding-Britton model*)



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.397389 (Hartree/Particle)

Thermal correction to Energy= 0.416463

Thermal correction to Enthalpy= 0.417328

Thermal correction to Gibbs Free Energy= 0.352253

Sum of electronic and zero-point Energies= -1154.094904

Sum of electronic and thermal Energies= -1154.075830

Sum of electronic and thermal Enthalpies= -1154.074966

Sum of electronic and thermal Free Energies= -1154.140041

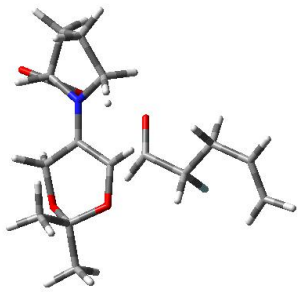
0 1

C	-0.32664800	0.84306800	0.83667200
H	-0.70438600	0.32024700	1.70806000
C	0.97307100	0.63587500	0.38879300
N	1.64143400	-0.47311900	0.70913000
C	2.88128900	-0.91022900	0.05978800
H	3.66798900	-0.16287000	0.20322100
C	1.30715400	-1.29487700	1.88779400
H	0.48519600	-1.97110100	1.64223100

H	0.99483100	-0.64174000	2.70757900
C	2.60997100	-2.03204200	2.18160700
H	2.43669500	-2.97967700	2.69616900
H	3.25991100	-1.41040700	2.80625600
C	3.22620500	-2.22040600	0.79667700
H	4.30352300	-2.39205900	0.81153300
H	2.74776600	-3.06382000	0.28631500
C	1.53675500	1.59617000	-0.62424600
H	2.44741300	2.06221800	-0.22054000
H	1.80912300	1.08495100	-1.55097500
O	-0.96780200	2.05017500	0.64695000
O	0.57574900	2.55606100	-1.00313800
C	-0.18013100	3.08809800	0.06423300
C	-1.15750700	4.06664400	-0.55272900
H	-0.61917900	4.91787900	-0.97816200
H	-1.85197900	4.43135100	0.20866200
C	0.69649300	3.73206400	1.13644200
H	1.29331900	2.99426100	1.68059700
H	0.06097500	4.24923700	1.86015000
H	1.37269800	4.45923700	0.67717400
C	-1.11487700	-0.44079500	-0.56352500
H	-1.02164000	0.29507700	-1.38146900
C	-2.51929700	-0.46457600	0.02559900
O	-0.48506700	-1.54031200	-0.61600400
C	2.80049100	-1.18468500	-1.44670700
O	1.63860700	-1.48291600	-1.98408400
O	3.82841600	-1.17525700	-2.09478100
H	0.82447200	-1.48985800	-1.34965600
H	-1.72415900	3.56836100	-1.34436100

C	-3.47551600	-1.18922400	-0.91790400
H	-3.43906000	-0.67198500	-1.88593400
C	-4.88417200	-1.20378900	-0.39708400
H	-2.86679900	0.55337600	0.22624800
H	-3.10362300	-2.20822800	-1.07026100
C	-5.56025800	-2.30735200	-0.08779800
H	-6.57973700	-2.26422800	0.28762600
H	-5.11818600	-3.29570600	-0.20181300
H	-5.35534400	-0.22886200	-0.26610300
F	-2.48969200	-1.15438800	1.24070300

TS-(*S*)- 2-fluoreopent-4-enal (*Polar Felkin-Anh model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.397497 (Hartree/Particle)

Thermal correction to Energy= 0.416522

Thermal correction to Enthalpy= 0.417387

Thermal correction to Gibbs Free Energy= 0.352587

Sum of electronic and zero-point Energies= -1154.092104

Sum of electronic and thermal Energies= -1154.073079

Sum of electronic and thermal Enthalpies= -1154.072214

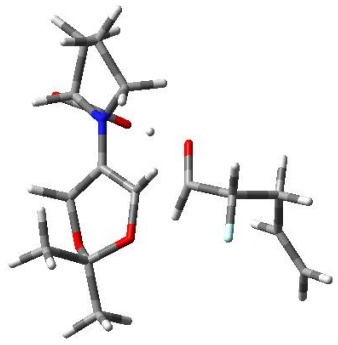
Sum of electronic and thermal Free Energies= -1154.137014

0 1

C	-0.57127400	0.62484800	0.74140300
H	-0.94434800	-0.02673200	1.52475700
C	0.78609600	0.65843100	0.43997100
N	1.58666200	-0.36687600	0.73575800
C	2.95328500	-0.51730100	0.22415500
H	3.56242800	0.34391200	0.51609600
C	1.27771200	-1.35321000	1.78771100
H	0.65538200	-2.14948300	1.37249400
H	0.73458900	-0.86394900	2.60081400
C	2.65545800	-1.85154300	2.21272000
H	2.61315800	-2.85355300	2.64499500
H	3.08715200	-1.16976900	2.95302900
C	3.45740200	-1.80176300	0.91366400
H	4.53774600	-1.76937500	1.06125500
H	3.21744100	-2.67168400	0.29199000
C	1.29746600	1.79131500	-0.40988800
H	2.09626100	2.32255400	0.12856400
H	1.72041200	1.42175800	-1.34801900

O	-1.36414900	1.74404100	0.58995300
O	0.25187100	2.65667900	-0.79058800
C	-0.67867500	2.94341300	0.23172500
C	-1.71612900	3.86032600	-0.38068500
H	-1.25755400	4.81562200	-0.64969000
H	-2.52085900	4.04316400	0.33614500
C	-0.02050400	3.55071600	1.46908600
H	0.62763600	2.83733500	1.98664100
H	-0.79625300	3.86997100	2.17010400
H	0.57697600	4.42152800	1.18310400
C	-0.97074000	-0.59906200	-0.88500700
H	-0.86498400	0.22787800	-1.60831200
C	-2.43869700	-0.85611300	-0.54148000
H	-2.90575000	0.04363600	-0.13366300
O	-0.18209400	-1.58827600	-0.93732000
C	3.09696100	-0.66660400	-1.29464700
O	2.07134800	-1.09298100	-1.99878900
O	4.17743000	-0.44013800	-1.80138600
H	1.20369500	-1.27731400	-1.48027000
H	-2.13383100	3.39629600	-1.27828400
C	-2.65592900	-2.06261900	0.34649000
H	-2.05607300	-1.93575400	1.25677000
C	-4.08178200	-2.32908400	0.74737500
H	-2.23705900	-2.94385500	-0.15419600
C	-5.17220100	-1.71208500	0.29609600
H	-5.13199600	-0.93034600	-0.45760600
H	-6.15829800	-1.98237600	0.66538500
H	-4.19746400	-3.11894600	1.48970000
F	-3.05344300	-1.08833200	-1.78991200

TS-(*S*)- 2-fluoreopent-4-enal *(Evans-Cornforth model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.396825 (Hartree/Particle)

Thermal correction to Energy= 0.415969

Thermal correction to Enthalpy= 0.416833

Thermal correction to Gibbs Free Energy= 0.351206

Sum of electronic and zero-point Energies= -1154.090846

Sum of electronic and thermal Energies= -1154.071703

Sum of electronic and thermal Enthalpies= -1154.070838

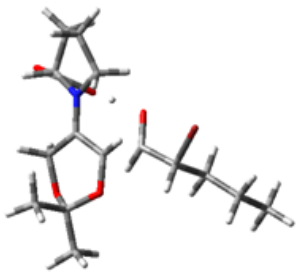
Sum of electronic and thermal Free Energies= -1154.136465

0 1

C	-0.38801200	0.81973200	0.97924300
H	-0.45080100	0.47085900	2.00533000
C	0.82613500	0.77880300	0.29453300
N	1.79578700	-0.06803000	0.63764000
C	2.98333700	-0.33351800	-0.18349000
H	3.53239600	0.59731800	-0.35693000
C	1.90849100	-0.66809400	1.98011700
H	1.30846000	-1.57997900	2.02299400
H	1.53998500	0.03821000	2.72881600
C	3.40166800	-0.94975800	2.11178400
H	3.60538200	-1.75570200	2.82010500
H	3.92449800	-0.04859300	2.44871700
C	3.81365600	-1.30102100	0.68355300
H	4.88059700	-1.18346300	0.48939100
H	3.53143400	-2.33499500	0.45584000
C	0.94221800	1.55729900	-0.98939800
H	1.79769600	2.24625500	-0.92708100
H	1.11511200	0.88817300	-1.83658000
O	-1.29728400	1.82854700	0.73276100
O	-0.25555100	2.23287800	-1.29165500
C	-0.88291300	2.83816900	-0.17965600
C	-2.15060600	3.47783100	-0.70663300
H	-2.73564200	3.88379900	0.12264700
H	-2.74793400	2.72753700	-1.23157900
C	0.02708300	3.84281100	0.52637700

H	0.87083000	3.35940700	1.02772300
H	-0.54879500	4.38173500	1.28366200
H	0.41828800	4.56376000	-0.19789800
C	-1.07226800	-0.90289300	0.07044900
H	-1.38918400	-0.34479000	-0.82662500
C	-2.21288800	-1.25478700	1.02327400
O	-0.17000700	-1.79613000	-0.00893500
C	2.73886800	-0.96372600	-1.56017300
O	1.61706600	-1.61058300	-1.78387400
O	3.62008400	-0.89052000	-2.39357000
H	0.93328000	-1.62838200	-1.01163100
H	-1.90300200	4.28904400	-1.39663800
C	-2.98182700	-2.48760700	0.53799800
H	-2.28125400	-3.32970600	0.55786400
C	-3.56368600	-2.32754500	-0.83926800
H	-1.80203900	-1.45280900	2.01868800
H	-3.77480700	-2.69092400	1.26634200
C	-4.86247100	-2.18993100	-1.09508600
H	-5.60436000	-2.19309100	-0.29819100
H	-5.23435600	-2.07216300	-2.11006000
H	-2.85173100	-2.31923900	-1.66464400
F	-3.10886100	-0.19601900	1.13185400

TS-(*R*)- 2-bromo pentanal (*Dudding-Britton model*)



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.418657 (Hartree/Particle)

Thermal correction to Energy= 0.438782

Thermal correction to Enthalpy= 0.439647

Thermal correction to Gibbs Free Energy= 0.371478

Sum of electronic and zero-point Energies= -3627.245748

Sum of electronic and thermal Energies= -3627.225622

Sum of electronic and thermal Enthalpies= -3627.224758

Sum of electronic and thermal Free Energies= -3627.292926

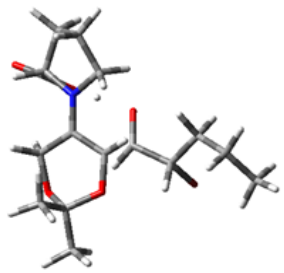
0 1

C	-0.19075600	0.89071100	-0.85399800
H	0.20387100	0.30144700	-1.67542900
C	-1.46595700	0.63803900	-0.35652800
N	-2.03714000	-0.55430300	-0.52207200

C	-3.22629600	-1.01484600	0.20295200
H	-4.08233200	-0.37386400	-0.02926200
C	-1.64234000	-1.48530800	-1.59717100
H	-0.74867600	-2.03736100	-1.29554000
H	-1.41407300	-0.91562400	-2.50280100
C	-2.86911000	-2.37781300	-1.75634700
H	-2.60948800	-3.36313500	-2.14929200
H	-3.58766700	-1.91030300	-2.43766800
C	-3.44369100	-2.44079800	-0.34279100
H	-4.49792000	-2.71923100	-0.30452100
H	-2.87251000	-3.15368600	0.26244200
C	-2.08987800	1.66526700	0.54905700
H	-3.04345100	2.00361400	0.11756300
H	-2.30068200	1.25040200	1.53776600
O	0.34789100	2.16156000	-0.83747700
O	-1.20370900	2.73745900	0.78189600
C	-0.51490400	3.19497500	-0.36280800
C	0.38550500	4.31912600	0.10437600
H	-0.21661500	5.16391100	0.44958400
H	1.02442300	4.65155600	-0.71790500
C	-1.46131700	3.62657400	-1.48110500
H	-1.99996200	2.77942900	-1.91611000
H	-0.88430100	4.10205900	-2.27871300
H	-2.19079400	4.34589900	-1.09675500
C	0.72084100	-0.11596700	0.67358800
H	0.56102800	0.71714900	1.38269000
C	2.14768800	-0.06481700	0.13173100
O	0.19156000	-1.24445700	0.89847500
C	-3.11288200	-1.07154600	1.73080300

O	-1.92620700	-1.20111600	2.28161600
O	-4.13315400	-1.05780800	2.39044600
H	-1.11864400	-1.21475900	1.64035600
H	1.01538300	3.96760700	0.92623200
C	3.14190600	-0.34781700	1.25510400
H	2.91294200	0.36706800	2.05840400
C	4.60928100	-0.19321200	0.85829900
H	4.85167800	-0.92261200	0.07719600
H	4.75980000	0.80143000	0.41802600
H	2.35048200	0.90338800	-0.32790500
H	2.95466500	-1.35043900	1.65739100
C	5.54859000	-0.37896300	2.04711900
H	5.42219000	-1.37053300	2.49817500
H	6.59608900	-0.28059200	1.74196900
H	5.35473500	0.36845500	2.82580200
Br	2.35396200	-1.38451100	-1.31830000

TS-(*S*)- 2-bromo pentanal (*Polar Felkin-Anh model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.418640 (Hartree/Particle)

Thermal correction to Energy= 0.438758

Thermal correction to Enthalpy= 0.439623

Thermal correction to Gibbs Free Energy= 0.371451

Sum of electronic and zero-point Energies= -3627.242421

Sum of electronic and thermal Energies= -3627.222303

Sum of electronic and thermal Enthalpies= -3627.221439

Sum of electronic and thermal Free Energies= -3627.289611

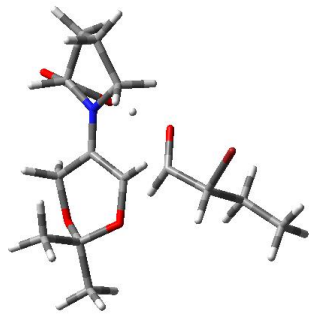
0 1

C	-0.26233000	0.86058700	-1.07118700
H	0.05721800	0.27924600	-1.93072500
C	-1.49372000	0.57519100	-0.47134300
N	-2.03195100	-0.63468400	-0.56337100
C	-3.13417800	-1.11369200	0.28133800
H	-4.01876900	-0.48781300	0.13103100
C	-1.70016600	-1.59311100	-1.63687300
H	-0.79300500	-2.13948400	-1.36883500
H	-1.52965700	-1.05136100	-2.57078800
C	-2.93012500	-2.49342900	-1.68815600
H	-2.69722800	-3.48001600	-2.09430100
H	-3.70516700	-2.03432800	-2.31063100
C	-3.38217800	-2.54706500	-0.23044800

H	-4.42667700	-2.83364200	-0.10062800
H	-2.75663900	-3.24979400	0.33112500
C	-2.08037700	1.59949900	0.46130200
H	-3.08328300	1.88079800	0.10734100
H	-2.18688200	1.20198100	1.47403600
O	0.20483600	2.15952800	-1.14307900
O	-1.22921600	2.71509400	0.58840700
C	-0.66036400	3.16846700	-0.62192900
C	0.22546200	4.34178300	-0.25954800
H	0.76928700	4.68584300	-1.14317600
H	0.94362400	4.03497500	0.50570000
C	-1.71515800	3.52839400	-1.66580100
H	-2.26143700	2.65015300	-2.02248700
H	-1.22697100	3.99195400	-2.52721700
H	-2.43247700	4.23824800	-1.24290800
C	0.79287800	-0.04334400	0.38214000
H	0.63281200	0.77650700	1.10313500
C	2.15252700	0.07963700	-0.30855700
O	0.33489100	-1.20304600	0.64524900
C	-2.86189700	-1.15055900	1.79068000
O	-1.62342700	-1.22867500	2.21868600
O	-3.81329700	-1.16689500	2.54686300
H	-0.87177200	-1.22142000	1.50073300
H	-0.38211800	5.16501300	0.12557600
C	2.53059600	-1.04550300	-1.26443800
H	1.69034100	-1.14885200	-1.96568800
C	2.84136700	-2.41542300	-0.65781300
H	3.74389200	-2.33870400	-0.04106700
H	2.02373600	-2.70783700	0.00526400

H	2.21958000	1.04824000	-0.80096500
H	3.38762400	-0.71255200	-1.86288500
C	3.04770200	-3.47059400	-1.74188000
H	2.13670700	-3.60836900	-2.33733000
H	3.85430400	-3.18542400	-2.42874700
H	3.30912200	-4.44019900	-1.30396000
Br	3.50334100	0.26390200	1.14508700

TS-(*S*)- 2-bromo butanal (*Dudding-Britton model*)



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.390015 (Hartree/Particle)

Thermal correction to Energy= 0.408882

Thermal correction to Enthalpy= 0.409746

Thermal correction to Gibbs Free Energy= 0.344877

Sum of electronic and zero-point Energies= -3587.970160

Sum of electronic and thermal Energies= -3587.951294

Sum of electronic and thermal Enthalpies= -3587.950429

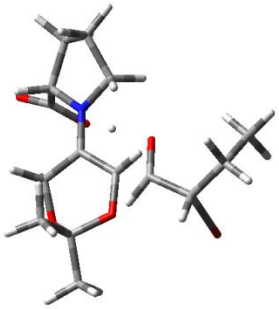
Sum of electronic and thermal Free Energies= -3588.015298

0 1

C	0.17649200	0.84626800	-0.78185000
H	0.64694200	0.21161700	-1.52584100
C	-1.16104500	0.66385700	-0.44472800
N	-1.76311400	-0.50863600	-0.64313000
C	-3.05776400	-0.88343300	-0.06471100
H	-3.83962700	-0.20344900	-0.41666600
C	-1.28025700	-1.50029000	-1.62324300
H	-0.47158300	-2.08802000	-1.18277800
H	-0.89622000	-0.97995400	-2.50538300
C	-2.52386600	-2.33127800	-1.92315500
H	-2.27113700	-3.34351700	-2.24602000
H	-3.11442100	-1.85198500	-2.71085600
C	-3.28783900	-2.31102200	-0.60054800
H	-4.35278900	-2.52495300	-0.70236000
H	-2.85270000	-3.03686500	0.09550500
C	-1.84601000	1.74927700	0.34115200
H	-2.70839200	2.12703600	-0.22720400
H	-2.21923500	1.37610900	1.29802200
O	0.77027700	2.09067200	-0.72946200
O	-0.93969100	2.77643600	0.67579900
C	-0.08463800	3.17777300	-0.37391000
C	0.81467600	4.25298400	0.19989700

H	0.22562300	5.13592600	0.46283100
H	1.57153900	4.53795400	-0.53529200
C	-0.85462800	3.64830000	-1.60604400
H	-1.37811900	2.82681000	-2.10437900
H	-0.15597100	4.08512700	-2.32469200
H	-1.58716800	4.40825400	-1.31847300
C	0.84047900	-0.15023700	0.87987800
H	0.63036000	0.71456200	1.53572700
C	2.32533300	-0.18239700	0.52588600
O	0.23360400	-1.24541800	1.06692200
C	-3.13862800	-0.89952300	1.46654400
O	-2.03698200	-1.06111000	2.16537800
O	-4.23116700	-0.82177200	1.99237200
H	-1.15712300	-1.13176600	1.63245300
H	1.31172000	3.87312800	1.09675700
C	3.14833500	-0.50251100	1.77267100
H	2.84743200	0.22676700	2.53700200
C	4.65643200	-0.41681900	1.56438400
H	5.18180100	-0.59344000	2.50863000
H	5.00002300	-1.16047900	0.83851900
H	4.94524100	0.57482200	1.19672100
H	2.64010900	0.76587700	0.08847500
H	2.86041300	-1.49165900	2.14471700
Br	2.65012400	-1.53638900	-0.87128400

TS-(*R*)- 2-bromo butanal (*Polar Felkin-Anh model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.389949 (Hartree/Particle)

Thermal correction to Energy= 0.408870

Thermal correction to Enthalpy= 0.409734

Thermal correction to Gibbs Free Energy= 0.344493

Sum of electronic and zero-point Energies= -3587.966453

Sum of electronic and thermal Energies= -3587.947532

Sum of electronic and thermal Enthalpies= -3587.946668

Sum of electronic and thermal Free Energies= -3588.011908

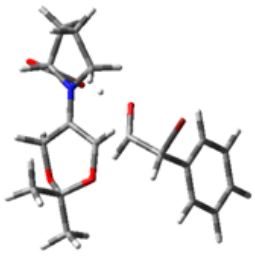
0 1

C	-0.04533000	0.87597200	-1.04139300
H	0.10440100	0.37978700	-1.99553600

C	-1.27949000	0.75631600	-0.39158000
N	-2.06977100	-0.28744800	-0.60795400
C	-3.20195800	-0.65056900	0.25418600
H	-3.92437700	0.17032700	0.28595900
C	-2.02060200	-1.11232100	-1.83158800
H	-1.25615800	-1.88424900	-1.71902100
H	-1.76870700	-0.48054500	-2.68712900
C	-3.42785900	-1.69458500	-1.91088600
H	-3.45181600	-2.62857100	-2.47635200
H	-4.10459100	-0.97851600	-2.38865300
C	-3.80549000	-1.88632200	-0.44292600
H	-4.88007700	-1.95066400	-0.26686400
H	-3.33502400	-2.79470200	-0.05048100
C	-1.58316700	1.71829500	0.72511400
H	-2.51330800	2.25983700	0.49789200
H	-1.72872400	1.19562300	1.67405600
O	0.67907300	2.05089300	-0.97120300
O	-0.50065500	2.59214800	0.94763500
C	0.08876000	3.11472500	-0.22388400
C	1.23316900	3.99435900	0.23389100
H	0.84703600	4.85559900	0.78558900
H	1.79746800	4.35193600	-0.63125100
C	-0.91507500	3.86064400	-1.09989700
H	-1.65621100	3.18884300	-1.54336200
H	-0.38400100	4.35904300	-1.91526400
H	-1.43870100	4.61582500	-0.50606900
C	0.86032000	-0.43057100	0.18276400
H	0.88454500	0.27161300	1.03347500
C	2.19894000	-0.44752800	-0.55801100

H	2.42854100	0.55759500	-0.90765600
O	0.19394900	-1.51262100	0.28632000
C	-2.85331200	-0.99949700	1.70698000
O	-1.64097400	-1.41110200	1.99468300
O	-3.73430800	-0.93764900	2.54223200
H	-0.94600200	-1.43698300	1.22004000
H	1.89836700	3.41805700	0.88288100
C	2.34683800	-1.46205400	-1.68648400
H	1.50330500	-1.29173200	-2.36886000
C	2.39050600	-2.93714300	-1.29480400
H	2.48190800	-3.55560900	-2.19422300
H	3.25247000	-3.14575700	-0.65326800
H	1.48540200	-3.22424500	-0.75697600
H	3.25187200	-1.20652700	-2.24928200
Br	3.60133200	-0.72815800	0.83028000

TS-(*R*)- 2-bromo phenylacetaldehyde (*Dudding-Britton model*)



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.415429 (Hartree/Particle)

Thermal correction to Energy= 0.435763

Thermal correction to Enthalpy= 0.436627

Thermal correction to Gibbs Free Energy= 0.367449

Sum of electronic and zero-point Energies= -3740.316934

Sum of electronic and thermal Energies= -3740.296601

Sum of electronic and thermal Enthalpies= -3740.295736

Sum of electronic and thermal Free Energies= -3740.364915

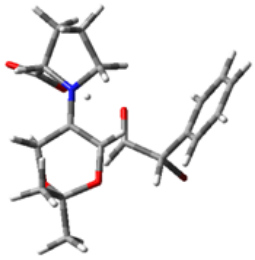
0 1

C	-0.71409800	1.01981600	-0.91328500
H	-0.47578100	0.53412000	-1.85382900
C	-1.83454600	0.63648500	-0.18422300
N	-2.38073300	-0.56773700	-0.35694500
C	-3.36773000	-1.17215200	0.54401800
H	-4.28044100	-0.56881000	0.56705400
C	-2.18793300	-1.35844900	-1.58834000
H	-1.22699600	-1.87701600	-1.54563100
H	-2.18658500	-0.68639400	-2.45145300
C	-3.37992500	-2.31019700	-1.58474000
H	-3.16717400	-3.23406300	-2.12693800
H	-4.24770700	-1.82766100	-2.04615200
C	-3.63494700	-2.54864000	-0.09803800
H	-4.64311000	-2.89906900	0.12758700
H	-2.91720800	-3.27913900	0.29175600
C	-2.28554700	1.52814600	0.94117100

H	-3.32291900	1.84741600	0.76402600
H	-2.25801800	1.00616500	1.90094800
O	-0.23267100	2.31112800	-0.87150600
O	-1.41229800	2.62508300	1.09610500
C	-1.00800400	3.23767600	-0.10987900
C	-0.06811300	4.35959900	0.27746300
H	-0.61037600	5.12866900	0.83416800
H	0.36386800	4.81020100	-0.61991100
C	-2.19130100	3.72184700	-0.94462600
H	-2.78588800	2.89185100	-1.33735800
H	-1.82090000	4.30159400	-1.79415200
H	-2.83890800	4.35991600	-0.33592600
C	0.54995400	-0.08507000	0.28481400
H	0.50638100	0.65700100	1.10194200
C	1.82323700	0.13408900	-0.53809500
O	0.12643100	-1.26108900	0.46775300
C	-2.92984300	-1.37347700	1.99918400
O	-1.64799600	-1.49143300	2.27250000
O	-3.78354200	-1.48434400	2.85576000
H	-1.00343300	-1.39347600	1.48025700
H	0.73715500	3.96379700	0.90262500
H	1.85567200	1.15431000	-0.91809700
Br	1.79100000	-1.02729600	-2.12877000
C	3.03871900	-0.14478700	0.31028100
C	3.28848400	-1.42163100	0.82356300
C	3.88616200	0.90967300	0.65290500
C	4.37474000	-1.63760200	1.66282700
H	2.62475100	-2.23920100	0.55970300
C	4.97449000	0.69250200	1.49682200

H	3.69458700	1.90448900	0.25846800
C	5.22038100	-0.58043400	2.00283200
H	4.56139900	-2.63219400	2.05737500
H	5.62909400	1.51945500	1.75638500
H	6.06816800	-0.75158200	2.65988500

TS-(*S*)- 2-bromo phenylacetaldehyde (*Polar Felkin-Anh model)*



%nprocshared=8

%mem=2500MB

freq wb97xd/6-31g(d) # opt=(calcfc,ts,noeigen) freq=noraman wb97xd/6-31g(d) scrf=(iefpcm,solvent=dichloromethane,smd) temperature=273

****

Thermochemistry

****

Zero-point correction= 0.415285 (Hartree/Particle)

Thermal correction to Energy= 0.435649

Thermal correction to Enthalpy= 0.436514

Thermal correction to Gibbs Free Energy= 0.367274

Sum of electronic and zero-point Energies= -3740.316811

Sum of electronic and thermal Energies= -3740.296447

Sum of electronic and thermal Enthalpies= -3740.295583

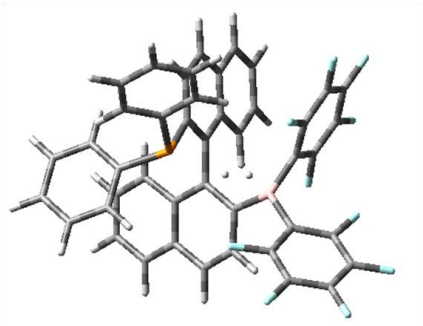
Sum of electronic and thermal Free Energies= -3740.364823

0 1

C	-0.41668800	0.76324800	-1.01137200
H	0.18715500	0.12140000	-1.64468300
C	-1.67031200	0.32758400	-0.58143100
N	-1.95152600	-0.96995800	-0.50010000
C	-3.12470100	-1.51624200	0.19316400
H	-4.04131600	-1.11633200	-0.25064600
C	-1.22597300	-2.00677100	-1.26079500
H	-0.33085900	-2.30496100	-0.71035200
H	-0.92765800	-1.60543100	-2.23266700
C	-2.24710100	-3.13391800	-1.36939500
H	-1.76855200	-4.10595100	-1.50615900
H	-2.91832000	-2.95240600	-2.21514600
C	-3.01343000	-3.03504200	-0.05191600
H	-3.99913900	-3.50160200	-0.07778000
H	-2.43267700	-3.49635400	0.75453100
C	-2.61659700	1.34885900	-0.00976900
H	-3.55189400	1.34769100	-0.58853500
H	-2.86924600	1.11993200	1.02894200
O	-0.17184400	2.09901700	-1.26230700
O	-2.01931100	2.62515800	0.02999800
C	-1.29103500	2.97577300	-1.12761100
C	-0.71946800	4.35412500	-0.87088700
H	-0.03804700	4.63059700	-1.67964700
C	-2.14372100	2.91953200	-2.39340000

H	-2.41565800	1.89439200	-2.66218200
H	-1.58266000	3.34836300	-3.22792200
H	-3.06090600	3.49826100	-2.24972600
C	0.45574300	0.36156600	0.78773400
H	0.03201500	1.26308500	1.26100800
C	1.88804900	0.61103300	0.29641800
H	1.92435600	1.53869300	-0.27203700
O	0.14813600	-0.78686700	1.22453200
C	-3.20669500	-1.24787000	1.70098600
O	-2.10586300	-0.98283000	2.36931100
O	-4.28659200	-1.34561100	2.24840000
H	-1.23571200	-0.92720200	1.82352800
H	-1.52471300	5.09202800	-0.81933500
C	2.51127700	-0.52335500	-0.46253400
C	2.72226700	-1.77621800	0.12360100
C	2.82279600	-0.34202700	-1.81187900
C	3.22282300	-2.82841800	-0.63490200
H	2.49397800	-1.91921100	1.17346300
C	3.32315800	-1.39781700	-2.57250600
H	2.66487700	0.63037000	-2.27239500
C	3.52164500	-2.64376800	-1.98538300
H	3.38166100	-3.79722300	-0.17013300
H	3.55857500	-1.24226800	-3.62125800
H	-0.17055400	4.35378400	0.07487700
Br	2.94586300	1.03588800	1.92945800
H	3.91235300	-3.46861700	-2.57428000

Hydrogen splitting transition state- B3LYP/6-31G(d)-Toluene solvent



%nprocshared=8

%mem=2500MB

opt=(calcfc,ts,noeigen) freq=noraman b3lyp/6-31g(d) scrf=(iefpcm,solvent=toluene,smd) temperature=300 pressure=1

****

Thermochemistry

****

Zero-point correction= 0.557498 (Hartree/Particle)

Thermal correction to Energy= 0.604383

Thermal correction to Enthalpy= 0.605333

Thermal correction to Gibbs Free Energy= 0.474201

Sum of electronic and zero-point Energies= -3055.103667

Sum of electronic and thermal Energies= -3055.056781

Sum of electronic and thermal Enthalpies= -3055.055831

Sum of electronic and thermal Free Energies= -3055.186964

0 1

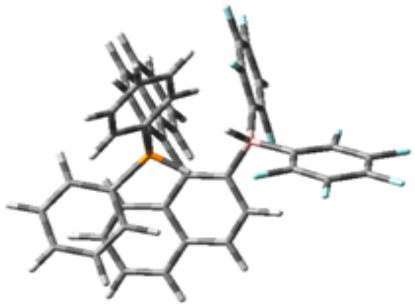
C	-1.79681800	0.86377800	0.82996400
C	-1.18157800	1.28573400	-0.35109600
C	-0.95749500	2.69349400	-0.56175700

C	-1.33836000	3.63237100	0.45364100
C	-1.94806000	3.15500400	1.64181400
C	-2.17150400	1.81326000	1.82228400
H	-0.06124000	2.51404200	-2.53007400
C	-0.36444500	3.20384800	-1.75222400
C	-1.10715900	5.01948000	0.24867600
H	-2.24435200	3.86930000	2.40628600
H	-2.64125400	1.46769600	2.73663500
C	-0.52936100	5.47520200	-0.91398200
C	-0.15509300	4.55518800	-1.92208200
H	-1.40035300	5.71500300	1.03129900
H	-0.35804100	6.53802700	-1.06118000
H	0.30270300	4.91809000	-2.83815700
C	-0.84597700	0.32831200	-1.47203300
C	-1.78995400	0.26893200	-2.56327300
C	0.34189200	-0.42119000	-1.51899200
C	-1.49663600	-0.53032100	-3.71657800
C	-3.02003600	0.98971400	-2.55761800
C	0.57522700	-1.22256200	-2.68009700
C	-2.41165200	-0.56648200	-4.80345100
C	-0.28784500	-1.26690100	-3.74411500
C	-3.89034300	0.93189400	-3.62376600
H	-3.27781900	1.59416100	-1.69614000
H	1.49121200	-1.80171900	-2.73435900
C	-3.58494600	0.15023300	-4.76316000
H	-2.16351200	-1.17587100	-5.66918900
H	-0.05668400	-1.87155500	-4.61803500
H	-4.82122900	1.49145700	-3.58935300
H	-4.27870700	0.11672500	-5.59890300

B	1.47139000	-0.46980600	-0.39095100
P	-2.02164100	-0.95011300	1.10686700
C	2.49128100	-1.71809300	-0.41487500
C	3.87631200	-1.58260000	-0.55392500
C	2.03929600	-3.03888400	-0.30300700
C	4.75300600	-2.66509800	-0.56592300
C	2.88118500	-4.14509100	-0.30214400
C	4.25292500	-3.95495200	-0.43438300
C	2.04191500	0.89563100	0.23633400
C	2.23415900	1.13049700	1.59851400
C	2.46125300	1.92957400	-0.60319100
C	2.74493000	2.32045900	2.10765900
C	2.98371300	3.13145800	-0.13941500
C	3.12418700	3.32973300	1.23008300
F	4.43739300	-0.36692800	-0.70740400
F	6.07236300	-2.47213300	-0.70819300
F	5.08229900	-5.00414200	-0.44215000
F	0.71901200	-3.28822200	-0.17958100
F	1.90729900	0.18065200	2.50774200
F	2.88581000	2.49461300	3.43050500
F	3.62268200	4.47967600	1.69963100
F	3.35402000	4.09302500	-0.99756300
F	2.38156300	1.77737400	-1.94129600
C	-3.61998200	-1.40350300	0.31303300
C	-3.70318200	-2.65589500	-0.31429100
C	-4.74690400	-0.56470000	0.31868000
C	-4.89434800	-3.06910500	-0.91447000
H	-2.83177900	-3.30525000	-0.33765500
C	-5.93476000	-0.97857000	-0.28498100

H	-4.69781700	0.41002400	0.79591100
C	-6.01036900	-2.23094600	-0.90084100
H	-4.94642600	-4.04115200	-1.39724000
H	-6.80123600	-0.32259900	-0.27530800
H	-6.93645000	-2.54980100	-1.37161700
F	2.38544000	-5.38514800	-0.18082400
C	-2.33330100	-1.11337500	2.91925100
C	-3.52798800	-1.62322000	3.44939200
C	-1.27867700	-0.80982900	3.80143700
C	-3.67029700	-1.81236900	4.82657100
H	-4.35308200	-1.87459200	2.79119200
C	-1.42871400	-0.98925400	5.17567000
H	-0.33798200	-0.42401700	3.41811800
C	-2.62502000	-1.49338900	5.69329300
H	-4.60373200	-2.20759400	5.21878300
H	-0.60668200	-0.74121800	5.84184300
H	-2.73804900	-1.63957700	6.76414200
H	0.01251400	-1.17049200	0.86981600
H	0.78387000	-0.97205100	0.92337700

Zwitterionic phosphonium -borohydride- B3LYP/6-31G(d)-Toluene solvent



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Thermochemistry

****

Zero-point correction= 0.562168 (Hartree/Particle)

Thermal correction to Energy= 0.609304

Thermal correction to Enthalpy= 0.610254

Thermal correction to Gibbs Free Energy= 0.477345

Sum of electronic and zero-point Energies= -3055.130129

Sum of electronic and thermal Energies= -3055.082993

Sum of electronic and thermal Enthalpies= -3055.082043

Sum of electronic and thermal Free Energies= -3055.214952

0 1

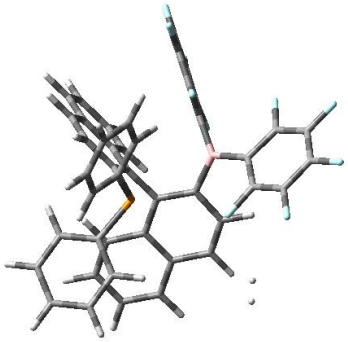
C -1.74454100 0.87181100 1.14552500

C	-1.06241600	1.57493600	0.15183600
C	-0.60387100	2.90155600	0.45866400
C	-0.88506500	3.47891400	1.74231900
C	-1.58882400	2.71582200	2.70991300
C	-1.99924200	1.43791700	2.42737500
H	0.38008200	3.24103800	-1.44298200
C	0.12734900	3.67837700	-0.48452800
C	-0.44782900	4.80127800	2.02243300
H	-1.78963700	3.15312400	3.68426300
H	-2.51317200	0.85639000	3.18638800
C	0.24532000	5.52736300	1.08114800
C	0.54039700	4.95608100	-0.18008000
H	-0.66943600	5.22680000	2.99786900
H	0.57545500	6.53777700	1.30585800
H	1.10385500	5.52878500	-0.91117300
C	-0.84026000	1.00749400	-1.22434900
C	-1.74355600	1.43666600	-2.26263900
C	0.22497400	0.13338400	-1.48087400
C	-1.53921200	0.96896700	-3.60213500
C	-2.84566500	2.31080800	-2.02938100
C	0.38122100	-0.29722400	-2.83445600
C	-2.41943200	1.38670400	-4.63650100
C	-0.44896800	0.09827100	-3.85398600
C	-3.68468600	2.69622000	-3.05302500
H	-3.02841200	2.68199900	-1.02635200
H	1.20391000	-0.96629000	-3.06877000
C	-3.47228300	2.23358700	-4.37328100
H	-2.24172400	1.02225500	-5.64581100
H	-0.28069900	-0.25160000	-4.87066200

H	-4.51665400	3.36403600	-2.84433000
H	-4.13819100	2.54867300	-5.17224900
B	1.20785600	-0.45453800	-0.30633100
P	-2.34946300	-0.79904100	0.82873400
C	1.92857000	-1.87057700	-0.74724100
C	3.16066100	-1.97470800	-1.39667600
C	1.32763600	-3.10121400	-0.47421000
C	3.77101300	-3.18388100	-1.72403800
C	1.89289100	-4.33533700	-0.78282500
C	3.13115700	-4.37741600	-1.41252100
C	2.30767300	0.61562200	0.28282900
C	2.71011900	0.55636300	1.61889200
C	2.91584100	1.63543300	-0.45010900
C	3.62193400	1.43401200	2.19987300
C	3.82852100	2.54053500	0.08523200
C	4.18801600	2.43797900	1.42378400
F	3.83154800	-0.85882500	-1.76678600
F	4.96142400	-3.20883400	-2.34896300
F	3.69532800	-5.55505300	-1.72401600
F	0.10844200	-3.15450800	0.12729300
F	2.20862000	-0.39776300	2.44558600
F	3.96080500	1.32073600	3.49794000
F	5.06832100	3.29867000	1.96069100
F	4.36661500	3.51035100	-0.67706300
F	2.62166700	1.80227500	-1.76069000
C	-4.02366700	-0.81719600	0.14322300
C	-4.31275600	-1.70597800	-0.90382700
C	-5.02157700	0.03450900	0.64304200
C	-5.59908200	-1.74478700	-1.44155400

H	-3.53918000	-2.35652200	-1.30236500
C	-6.30383100	-0.01256500	0.09900400
H	-4.79798600	0.73530000	1.44207000
C	-6.59223100	-0.90080100	-0.94072900
H	-5.82129300	-2.42833300	-2.25557600
H	-7.07554000	0.64842700	0.48243500
H	-7.59168300	-0.92984800	-1.36542700
F	1.25558000	-5.48279100	-0.48430500
C	-2.26154400	-1.80357400	2.33755300
C	-3.36881600	-2.55328400	2.76029100
C	-1.05029300	-1.86454200	3.04970900
C	-3.26587300	-3.35983400	3.89435700
H	-4.30438800	-2.51139700	2.21243800
C	-0.96106200	-2.67523700	4.17955300
H	-0.18734100	-1.29041300	2.72675400
C	-2.06456100	-3.42179700	4.60164600
H	-4.12456900	-3.93916800	4.22073900
H	-0.02527000	-2.72470600	4.72827500
H	-1.98633100	-4.05205200	5.48309000
H	-1.55176200	-1.39238300	-0.14782500
H	0.50458300	-0.73584200	0.64138700

Hydrogen splitting starting material- B3LYP/6-31G(d)-Toluene solvent



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Thermochemistry

****

Zero-point correction= 0.554343 (Hartree/Particle)

Thermal correction to Energy= 0.604327

Thermal correction to Enthalpy= 0.605277

Thermal correction to Gibbs Free Energy= 0.465816

Sum of electronic and zero-point Energies= -3055.130393

Sum of electronic and thermal Energies= -3055.080408

Sum of electronic and thermal Enthalpies= -3055.079458

Sum of electronic and thermal Free Energies= -3055.218919

0 1

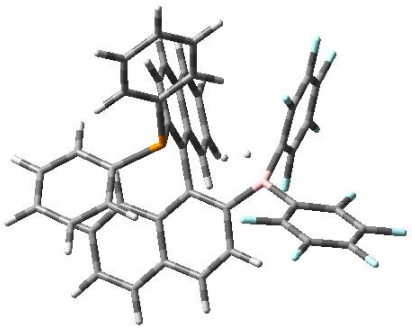
C	-1.44799000	0.55971900	1.08615300
C	-1.10076300	1.31100600	-0.04118300

C	-0.91721700	2.73521700	0.08099200
C	-1.03428000	3.35784000	1.36754500
C	-1.34684200	2.55394700	2.49333100
C	-1.55332800	1.20445000	2.35297400
H	-0.51145300	3.12112800	-2.01666900
C	-0.61279300	3.56705900	-1.03468400
C	-0.84056500	4.76039400	1.48951500
H	-1.43360600	3.02481200	3.46976400
H	-1.80336700	0.61074500	3.22555500
C	-0.54766800	5.53198000	0.38798200
C	-0.43451300	4.92546600	-0.88544500
H	-0.93093400	5.21247700	2.47431700
H	-0.40299100	6.60388600	0.49165800
H	-0.20324000	5.53622000	-1.75382500
C	-0.97903800	0.69098200	-1.41152800
C	-2.10161700	0.80386000	-2.30320000
C	0.18661400	0.02530900	-1.82707600
C	-2.01422000	0.26120500	-3.62917400
C	-3.31598700	1.45025000	-1.92808200
C	0.21861100	-0.53220100	-3.14543300
C	-3.11633100	0.39430200	-4.51552100
C	-0.82521800	-0.40266300	-4.02328600
C	-4.36664700	1.56416200	-2.81029700
H	-3.41224300	1.85616400	-0.92803400
H	1.11482400	-1.05407700	-3.46828100
C	-4.26838000	1.03364600	-4.11906400
H	-3.03013300	-0.02175000	-5.51642900
H	-0.75937500	-0.81583000	-5.02677600
H	-5.28103000	2.06119800	-2.49856400

H	-5.10519800	1.12981400	-4.80550000
B	1.48805900	-0.14928300	-0.97968100
P	-1.80799600	-1.26259000	0.90567300
C	2.31495500	-1.49450800	-1.05196500
C	3.71898300	-1.51442500	-0.97616600
C	1.71653500	-2.75898300	-1.18964100
C	4.47398000	-2.68014200	-1.02720700
C	2.44033400	-3.94580200	-1.22660800
C	3.82828500	-3.90617900	-1.14933800
C	2.10398900	1.02998500	-0.12608300
C	2.48959900	0.87936800	1.20718000
C	2.37214200	2.27661100	-0.69464500
C	3.05569000	1.90358000	1.95558100
C	2.95511300	3.32240400	0.01269600
C	3.29096200	3.13530000	1.34964500
F	4.41583300	-0.36853400	-0.87966000
F	5.81117700	-2.63250000	-0.96695000
F	4.53513200	-5.03609800	-1.19653400
F	0.38295900	-2.88196700	-1.27062100
F	2.30644700	-0.30806400	1.82443600
F	3.38493900	1.71654400	3.24114400
F	3.84093800	4.13193800	2.05010100
F	3.19043400	4.50149400	-0.57818800
F	2.09706200	2.49261600	-1.99567700
C	-3.63681800	-1.27252900	0.59456600
C	-4.12769700	-2.27010000	-0.26265400
C	-4.54666600	-0.35814200	1.15220500
C	-5.49200900	-2.36041000	-0.54910600
H	-3.43561400	-2.97730000	-0.71319800

C	-5.90886700	-0.44369600	0.86131400
H	-4.19211000	0.42693800	1.81399300
C	-6.38481600	-1.44599400	0.01125300
H	-5.85366900	-3.13980700	-1.21470200
H	-6.59980700	0.27196900	1.29986900
H	-7.44593600	-1.51012700	-0.21517000
F	1.81415000	-5.12468500	-1.34446200
C	-1.68428200	-1.88450000	2.64927300
C	-2.75174200	-2.48683100	3.33303200
C	-0.41747000	-1.87874600	3.26328800
C	-2.56105100	-3.05739800	4.59480500
H	-3.73926500	-2.51482300	2.88397600
C	-0.23218800	-2.43501000	4.52820600
H	0.42934800	-1.42761300	2.75371300
C	-1.30401200	-3.03115000	5.19863700
H	-3.40220500	-3.51965200	5.10547700
H	0.75293700	-2.40971300	4.98722400
H	-1.15802300	-3.47363800	6.18051200
H	-0.58808500	-5.04312300	-2.51325700
H	-1.10946800	-5.39111900	-2.91137600

Hydrogen splitting transition state- B3LYP/6-31G(d)- Dichloromethane solvent



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Thermochemistry

****

Zero-point correction= 0.556982 (Hartree/Particle)

Thermal correction to Energy= 0.603949

Thermal correction to Enthalpy= 0.604899

Thermal correction to Gibbs Free Energy= 0.473728

Sum of electronic and zero-point Energies= -3055.111151

Sum of electronic and thermal Energies= -3055.064183

Sum of electronic and thermal Enthalpies= -3055.063233

Sum of electronic and thermal Free Energies= -3055.194405

0 1

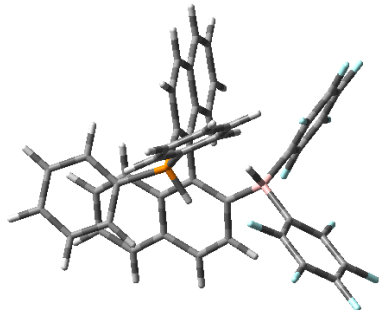
C	-1.79625400	0.85552000	0.84147800
C	-1.18341900	1.28752400	-0.33701500
C	-0.96088800	2.69716100	-0.53740800
C	-1.33908500	3.62733600	0.48718300

C	-1.94585100	3.14032300	1.67340400
C	-2.16932800	1.79669900	1.84235600
H	-0.07435800	2.53663700	-2.51277400
C	-0.37396800	3.21874800	-1.72651600
C	-1.11051000	5.01700300	0.29328900
H	-2.24102700	3.84869100	2.44369400
H	-2.64041300	1.44411000	2.75329100
C	-0.53840600	5.48368300	-0.86843800
C	-0.16773600	4.57230100	-1.88649700
H	-1.40226700	5.70480700	1.08320100
H	-0.37008600	6.54807700	-1.00802100
H	0.28345800	4.94404300	-2.80248900
C	-0.84769900	0.33863600	-1.46502600
C	-1.79195500	0.28517300	-2.55655300
C	0.34012300	-0.41079800	-1.51699100
C	-1.49902800	-0.50789100	-3.71462900
C	-3.02308500	1.00523700	-2.54579600
C	0.57422000	-1.20533300	-2.68327600
C	-2.41521400	-0.53971700	-4.80144100
C	-0.28953400	-1.24397800	-3.74780200
C	-3.89464000	0.95207400	-3.61193700
H	-3.28163900	1.60450500	-1.68074200
H	1.49010400	-1.78454600	-2.74136300
C	-3.58960400	0.17592600	-4.75608000
H	-2.16691600	-1.14481800	-5.67012000
H	-0.05936500	-1.84352800	-4.62548200
H	-4.82614300	1.51047300	-3.57395200
H	-4.28452200	0.14603900	-5.59102300
B	1.47045000	-0.46693700	-0.38906300

P	-2.02539000	-0.96108200	1.10196100
C	2.48752100	-1.71759900	-0.42215700
C	3.87147100	-1.58539700	-0.57048300
C	2.03425400	-3.03757300	-0.31214400
C	4.74541000	-2.66935200	-0.59172400
C	2.87336200	-4.14528300	-0.32014800
C	4.24408300	-3.95820000	-0.46094500
C	2.04963100	0.89559600	0.23813200
C	2.25568200	1.12316800	1.59969700
C	2.46341800	1.93323900	-0.59909600
C	2.77403000	2.30934000	2.10965200
C	2.99209600	3.13159100	-0.13402500
C	3.14653900	3.32259400	1.23453300
F	4.43575200	-0.36998600	-0.72407400
F	6.06518800	-2.47810000	-0.74251700
F	5.07174900	-5.00961000	-0.47741700
F	0.71331200	-3.28589400	-0.18258200
F	1.93723600	0.17001600	2.50769500
F	2.92923000	2.47595500	3.43253100
F	3.65242200	4.46955400	1.70537100
F	3.35623400	4.09747300	-0.99186400
F	2.37343100	1.78953800	-1.93846800
C	-3.62905700	-1.39531800	0.30636800
C	-3.72411000	-2.64293000	-0.32999100
C	-4.74772000	-0.54487100	0.31613500
C	-4.91824200	-3.03902100	-0.93711800
H	-2.86101000	-3.30354900	-0.35464600
C	-5.93850100	-0.94155800	-0.29454000
H	-4.69080600	0.42514300	0.80193400

C	-6.02571500	-2.18866800	-0.92070900
H	-4.97957500	-4.00736100	-1.42636700
H	-6.79804600	-0.27656300	-0.28158100
H	-6.95369000	-2.49394500	-1.39678000
F	2.37496400	-5.38530900	-0.19976000
C	-2.33325000	-1.14098900	2.91361500
C	-3.53316600	-1.64018900	3.44281000
C	-1.27120400	-0.86097800	3.79504400
C	-3.67311400	-1.84224800	4.81891100
H	-4.36485300	-1.87283600	2.78596700
C	-1.41837700	-1.05307700	5.16839600
H	-0.32734200	-0.48328900	3.41138500
C	-2.61987900	-1.54701100	5.68537600
H	-4.61064600	-2.22855600	5.21029900
H	-0.59077300	-0.82299500	5.83423700
H	-2.73102200	-1.70325600	6.75504400
H	0.02817100	-1.16051500	0.86197700
H	0.79591900	-0.96395300	0.93263000

Zwitterionic phosphonium -borohydride- B3LYP/6-31G(d) -Dichloromethane solvent



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Thermochemistry

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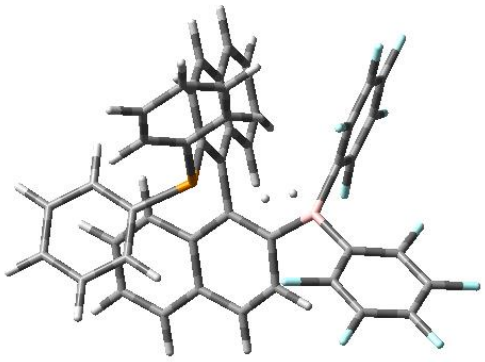
C	-1.77909500	0.83889200	1.13529400
C	-1.07108300	1.54619100	0.16272200
C	-0.60940100	2.86764100	0.49051800
C	-0.90334400	3.43147600	1.77741800
C	-1.62931100	2.66403400	2.72467200
C	-2.05089000	1.39515700	2.41804900
H	0.39037700	3.23503200	-1.39954600
C	0.13343400	3.65622500	-0.43475200
C	-0.46159000	4.74785700	2.08115400
H	-1.84404300	3.09262400	3.69987600
H	-2.59284400	0.81520700	3.15817400

C	0.24452400	5.48434300	1.15735800
C	0.54798500	4.92891800	-0.10961700
H	-0.69399900	5.16027000	3.05965700
H	0.57567200	6.49067500	1.39849000
H	1.11672500	5.51118100	-0.82929300
C	-0.82458000	0.99535400	-1.21687900
C	-1.72112000	1.42391900	-2.26122700
C	0.25429300	0.13786900	-1.47265800
C	-1.49754500	0.97299700	-3.60381900
C	-2.83601800	2.28319300	-2.02978400
C	0.42984900	-0.27747800	-2.82906600
C	-2.37209300	1.39109300	-4.64379900
C	-0.39459200	0.11758900	-3.85431600
C	-3.66920800	2.66939600	-3.05846200
H	-3.03467400	2.64007500	-1.02461100
H	1.26153100	-0.93623900	-3.06252600
C	-3.43789500	2.22276300	-4.38191700
H	-2.18011400	1.03837600	-5.65468400
H	-0.21359600	-0.22134300	-4.87251400
H	-4.51208400	3.32385500	-2.85137800
H	-4.10035000	2.53765400	-5.18386300
B	1.23387600	-0.44745200	-0.29445200
P	-2.42081100	-0.81669400	0.79139100
C	1.97017500	-1.85768000	-0.73425500
C	3.19656200	-1.94915800	-1.39555000
C	1.39133400	-3.09581700	-0.44517000
C	3.82303900	-3.14995400	-1.72050700
C	1.97430800	-4.32263100	-0.75077300
C	3.20620400	-4.35067200	-1.39278500

C	2.33348300	0.62447300	0.30023700
C	2.73305000	0.56224900	1.63743600
C	2.94612100	1.64570900	-0.42678700
C	3.64451700	1.43706700	2.22302100
C	3.85863300	2.54802200	0.11306900
C	4.21424600	2.44229000	1.45196100
F	3.84777600	-0.82471800	-1.78264400
F	5.00863000	-3.15994000	-2.35756300
F	3.78657900	-5.52210300	-1.70060100
F	0.18191000	-3.16411700	0.17027300
F	2.22991400	-0.39389800	2.46052700
F	3.98070100	1.31903400	3.52185300
F	5.09554400	3.29984300	1.99331400
F	4.40224400	3.51777400	-0.64694900
F	2.66037400	1.81659800	-1.74001400
C	-4.08733300	-0.78274100	0.09254200
C	-4.37747500	-1.61401700	-1.00077300
C	-5.07899700	0.05323500	0.63128000
C	-5.66040500	-1.60901800	-1.54906300
H	-3.60891100	-2.25489300	-1.42366500
C	-6.35726200	0.04963900	0.07539700
H	-4.85464800	0.70458600	1.47092000
C	-6.64750500	-0.77933000	-1.01248400
H	-5.88480900	-2.24838100	-2.39777100
H	-7.12487300	0.69727100	0.48873300
H	-7.64422300	-0.77494400	-1.44467600
F	1.36004000	-5.47841600	-0.43495200
C	-2.35796600	-1.84420600	2.28600200
C	-3.46900400	-2.61111600	2.66604100

C	-1.16689000	-1.90459000	3.03123600
C	-3.38883100	-3.43502900	3.78994000
H	-4.38975700	-2.56936300	2.09388500
C	-1.09952300	-2.73229400	4.15056800
H	-0.30302900	-1.31321200	2.74396400
C	-2.20721300	-3.49619000	4.53037000
H	-4.25099000	-4.02676900	4.08325300
H	-0.17984700	-2.77970800	4.72625600
H	-2.14761700	-4.13853100	5.40452500
H	-1.62588800	-1.40759100	-0.19055100
H	0.52779800	-0.73272200	0.64850000

Hydrogen splitting transition state- B3LYP/6-31G(d)- Diethylether solvent



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%mem=2500MB

opt=(calcfc,ts,noeigen) freq=noraman b3lyp/6-31g(d) scrf=(iefpcm,solvent=diethylether,smd) temperature=300

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Thermochemistry

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Zero-point correction= 0.556982 (Hartree/Particle)

Thermal correction to Energy= 0.603949

Thermal correction to Enthalpy= 0.604899

Thermal correction to Gibbs Free Energy= 0.473728

Sum of electronic and zero-point Energies= -3055.111151

Sum of electronic and thermal Energies= -3055.064183

Sum of electronic and thermal Enthalpies= -3055.063233

Sum of electronic and thermal Free Energies= -3055.194405

0 1

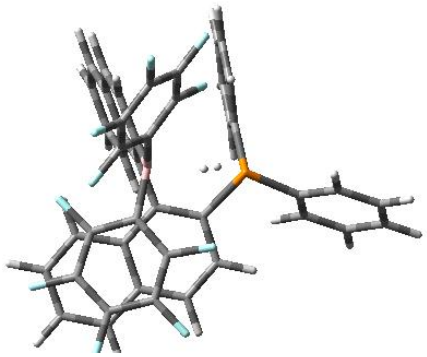
C	-1.79625400	0.85552000	0.84147800
C	-1.18341900	1.28752400	-0.33701500
C	-0.96088800	2.69716100	-0.53740800
C	-1.33908500	3.62733600	0.48718300
C	-1.94585100	3.14032300	1.67340400
C	-2.16932800	1.79669900	1.84235600
H	-0.07435800	2.53663700	-2.51277400
C	-0.37396800	3.21874800	-1.72651600
C	-1.11051000	5.01700300	0.29328900
H	-2.24102700	3.84869100	2.44369400
H	-2.64041300	1.44411000	2.75329100
C	-0.53840600	5.48368300	-0.86843800
C	-0.16773600	4.57230100	-1.88649700
H	-1.40226700	5.70480700	1.08320100
H	-0.37008600	6.54807700	-1.00802100
H	0.28345800	4.94404300	-2.80248900
C	-0.84769900	0.33863600	-1.46502600
C	-1.79195500	0.28517300	-2.55655300

C	0.34012300	-0.41079800	-1.51699100
C	-1.49902800	-0.50789100	-3.71462900
C	-3.02308500	1.00523700	-2.54579600
C	0.57422000	-1.20533300	-2.68327600
C	-2.41521400	-0.53971700	-4.80144100
C	-0.28953400	-1.24397800	-3.74780200
C	-3.89464000	0.95207400	-3.61193700
H	-3.28163900	1.60450500	-1.68074200
H	1.49010400	-1.78454600	-2.74136300
C	-3.58960400	0.17592600	-4.75608000
H	-2.16691600	-1.14481800	-5.67012000
H	-0.05936500	-1.84352800	-4.62548200
H	-4.82614300	1.51047300	-3.57395200
H	-4.28452200	0.14603900	-5.59102300
B	1.47045000	-0.46693700	-0.38906300
P	-2.02539000	-0.96108200	1.10196100
C	2.48752100	-1.71759900	-0.42215700
C	3.87147100	-1.58539700	-0.57048300
C	2.03425400	-3.03757300	-0.31214400
C	4.74541000	-2.66935200	-0.59172400
C	2.87336200	-4.14528300	-0.32014800
C	4.24408300	-3.95820000	-0.46094500
C	2.04963100	0.89559600	0.23813200
C	2.25568200	1.12316800	1.59969700
C	2.46341800	1.93323900	-0.59909600
C	2.77403000	2.30934000	2.10965200
C	2.99209600	3.13159100	-0.13402500
C	3.14653900	3.32259400	1.23453300
F	4.43575200	-0.36998600	-0.72407400

F	6.06518800	-2.47810000	-0.74251700
F	5.07174900	-5.00961000	-0.47741700
F	0.71331200	-3.28589400	-0.18258200
F	1.93723600	0.17001600	2.50769500
F	2.92923000	2.47595500	3.43253100
F	3.65242200	4.46955400	1.70537100
F	3.35623400	4.09747300	-0.99186400
F	2.37343100	1.78953800	-1.93846800
C	-3.62905700	-1.39531800	0.30636800
C	-3.72411000	-2.64293000	-0.32999100
C	-4.74772000	-0.54487100	0.31613500
C	-4.91824200	-3.03902100	-0.93711800
H	-2.86101000	-3.30354900	-0.35464600
C	-5.93850100	-0.94155900	-0.29454000
H	-4.69080600	0.42514300	0.80193400
C	-6.02571500	-2.18866900	-0.92070900
H	-4.97957500	-4.00736100	-1.42636700
H	-6.79804600	-0.27656400	-0.28158100
H	-6.95369000	-2.49394600	-1.39678000
F	2.37496400	-5.38530900	-0.19976000
C	-2.33325000	-1.14098900	2.91361500
C	-3.53316600	-1.64018900	3.44281000
C	-1.27120400	-0.86097800	3.79504400
C	-3.67311400	-1.84224800	4.81891100
H	-4.36485300	-1.87283600	2.78596700
C	-1.41837700	-1.05307700	5.16839600
H	-0.32734200	-0.48328900	3.41138500
C	-2.61987900	-1.54701100	5.68537600
H	-4.61064600	-2.22855600	5.21029900

H	-0.59077300	-0.82299500	5.83423700
H	-2.73102200	-1.70325600	6.75504400
H	0.02817100	-1.16051500	0.86197700
H	0.79591900	-0.96395300	0.93263000

Hydrogen splitting transition state- B3LYP-D3/6-31G(d)-Toluene solvent



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%mem=2500MB

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Thermochemistry

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Zero-point correction= 0.558256 (Hartree/Particle)

Thermal correction to Energy= 0.604717

Thermal correction to Enthalpy= 0.605667

Thermal correction to Gibbs Free Energy= 0.478455

Sum of electronic and zero-point Energies= -3055.220986

Sum of electronic and thermal Energies= -3055.174525

Sum of electronic and thermal Enthalpies= -3055.173575

Sum of electronic and thermal Free Energies= -3055.300787

0 1

C	1.78916700	0.84719200	-0.64792300
C	1.10266800	1.06267900	0.54843800
C	0.85353800	2.40483900	1.00202800
C	1.23401600	3.51198000	0.17855400
C	1.86130600	3.25239200	-1.06660000
C	2.13411900	1.96722600	-1.46166900
H	-0.13111000	1.85821900	2.85737000
C	0.19280600	2.68223400	2.23269300
C	0.94031000	4.83531400	0.60335900
H	2.12262200	4.08899800	-1.70977000
H	2.61232100	1.80377300	-2.42059200
C	0.30300700	5.06700200	1.80161700
C	-0.07064200	3.97693800	2.62305100
H	1.22159800	5.66271500	-0.04347500
H	0.07524400	6.08239900	2.11352200
H	-0.58842700	4.16166300	3.55990700
C	0.62355100	-0.07500700	1.40164100
C	1.40380800	-0.39431300	2.56535500
C	-0.55044000	-0.78616500	1.10185200
C	1.00445200	-1.47752600	3.41135900
C	2.57843400	0.32975300	2.91943800
C	-0.90807800	-1.86014000	1.97637000
C	1.78195600	-1.79843800	4.55631700

C	-0.16759800	-2.20056000	3.07945300
C	3.30229400	0.00899300	4.04586900
H	2.90712400	1.14750900	2.28889600
H	-1.81724200	-2.41764800	1.78055100
C	2.90534000	-1.06908400	4.87273200
H	1.46726000	-2.63058200	5.18140500
H	-0.47956600	-3.02261800	3.71922600
H	4.19205400	0.58041300	4.29606800
H	3.49047200	-1.31867400	5.75375500
B	-1.56549700	-0.42306500	-0.06828300
P	2.00912600	-0.85187100	-1.34962700
C	-2.78120800	-1.42922300	-0.36394800
C	-4.12762600	-1.05050800	-0.34237700
C	-2.55367900	-2.77815600	-0.66835600
C	-5.17271400	-1.93707500	-0.59508500
C	-3.56692500	-3.69120100	-0.93335900
C	-4.89113500	-3.26431000	-0.89616800
C	-1.76082000	1.11914700	-0.45515300
C	-1.36495900	1.76274900	-1.62758700
C	-2.32197100	1.94734200	0.51717100
C	-1.47975200	3.13858500	-1.80842000
C	-2.47024300	3.31922900	0.36885000
C	-2.03214500	3.92297200	-0.80417200
F	-4.48753200	0.21280200	-0.05012400
F	-6.44574500	-1.51922000	-0.55181000
F	-5.88262900	-4.12559100	-1.14546600
F	-1.28960100	-3.24885100	-0.72589000
F	-0.78662200	1.08213800	-2.64035500
F	-1.02149000	3.71728700	-2.92995900

F	-2.11097400	5.25187100	-0.95100200
F	-2.96789700	4.06878800	1.36354800
F	-2.71066200	1.40783200	1.69377400
C	2.75049400	-1.92099600	-0.04389900
C	2.07124400	-3.11497000	0.24297200
C	3.93896400	-1.63083000	0.64355600
C	2.56568700	-3.99975600	1.20293600
H	1.14011800	-3.33989700	-0.26797300
C	4.43043900	-2.51453300	1.60324000
H	4.47301600	-0.70686200	0.44772900
C	3.74455200	-3.69946000	1.88623800
H	2.02271200	-4.91508700	1.42227300
H	5.34179000	-2.27166400	2.14290900
H	4.12702300	-4.38134300	2.64090600
F	-3.28302900	-4.96863900	-1.22444900
C	3.37211500	-0.68765100	-2.58161000
C	4.57155700	0.00949000	-2.35142400
C	3.20296300	-1.35511600	-3.80416600
C	5.57564700	0.02976000	-3.31828400
H	4.71319800	0.55561500	-1.42403400
C	4.21162200	-1.33865700	-4.77103400
H	2.27768200	-1.89093900	-4.00024800
C	5.39899900	-0.64748400	-4.52904000
H	6.49601500	0.57564500	-3.12791700
H	4.06546100	-1.86174300	-5.71225100
H	6.18315500	-0.63044800	-5.28131100
H	-0.93412200	-0.94490100	-1.53613000
H	-0.16288500	-1.04485100	-1.52829000